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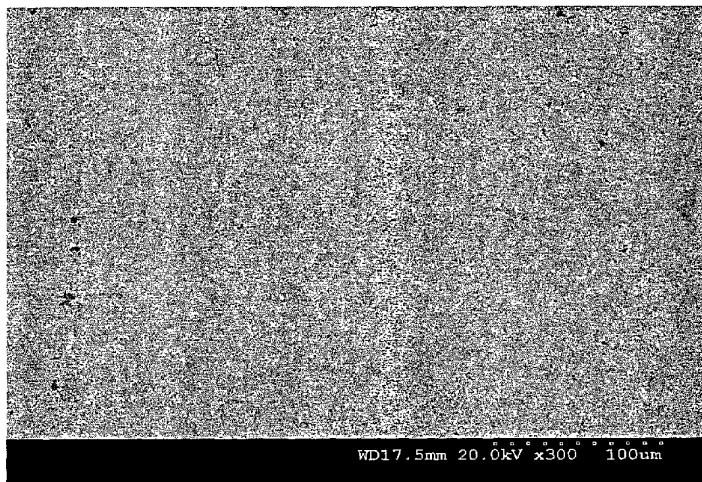
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(54) Title: COMPOSITE COMBINING MONOLAYER OR MULTILAYER OF ZEOLITE MOLECULAR SIEVE OR ITS ANALOGUE ONTO A SUBSTRATE AND PREPARATION THEREOF



(57) Abstract: The present invention relates to a zeolite-substrate composite having a zeolite monolayer or multilayer bound on the surface of the substrate, comprising (i) a substrate selected from a group consisting of a substrate having surface hydroxyl groups, a metal substrate capable of reacting with thiol groups, and a polymeric materials having reactive functional groups at its main or side chain, (ii) molecular sieve particles selected from porous oxides or sulfides having surface hydroxyl groups, and (iii) a linker derived from a linking compound having at least two functional groups at both terminal ends, of which one is chemically bonded to said substrate and the other is chemically bonded to said zeolite; wherein said chemical bonding of linker to the substrate and zeolite or its analog is achieved by any of covalent bonds, ionic bonds, and/or coordination bonds, and a method of preparing the same.



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COMPOSITE COMBINING MONOLAYER OR MULTILAYER OF ZEOLITE MOLECULAR SIEVE  
OR ITS ANALOGUE ONTO A SUBSTRATE AND PREPARATION THEREOF

TECHNICAL FIELD

The present invention relates to a zeolite-substrate composite which is formed by combining a monolayer or multilayer of zeolite or various type of molecular sieve bound onto the surface of a substrate by means of chemical bonding and a process for the preparation of the same.

BACKGROUND ART

Molecular sieve (hereinafter, often referred to as MS) such as various kinds of zeolites is a very useful material which is widely used in industry and in household item level. MS is generally present in the form of fine powder, which gives both advantages and disadvantages for using them.

In the present invention, fine particles of MS are applied and bonded in the form of a mono- or multi-layer on the surface of a substrate (or support) through chemical bond. By doing so, a wide applicability of MS is expected.

"Zeolite" is a generic name of crystalline aluminosilicate, which constitutes the pore skeleton of zeolite molecules and bears an anionic charge for each aluminum atom. Cations for offsetting such anion charges are present within the pore space and the remaining pore space is filled with water. The three dimensional pore structure of the zeolite molecule varies depending on the shape and size of the pore, and the pore diameter is usually determined by size of the molecule. Therefore, based on the shape and size of the pore, zeolite has a shape selectivity for a molecule entering into the pore. In this

connection, zeolite is called as a molecular sieve.

Zeolite shows diverse chemical and physical properties depending on its chemical composition, structure, pre-treatment method, etc. Especially, modified zeolite in which protons are replaced with other cations is widely used as a cracking catalyst of crude oil in the petrochemical industry, thanks to its resistance to high temperature. Further, zeolite is widely used as a water-absorbing drying agent, adsorbent, gas-purifying agent, ion exchanger, additives for detergent, soil improving agent or the like. An extensive study is now being made on its application as a sensor carrier.

Meanwhile, there are many known zeolite-like molecular sieves wherein a part or all of silicon (Si) and/or aluminum (Al) atoms constituting the structural skeleton of zeolite molecule are replaced with other elements. Such zeolite-like molecular sieves may be referred to as zeotype molecular sieves.

For example, a mesoporous silica (MCM-series mesoporous silica and silicalite, etc.) in which aluminum atoms are completely eliminated, an alpo( $\text{AlPO}_4$ )-type molecular sieve in which silicon atoms are replaced with phosphorous atoms, and other molecular sieve or its analog wherein skeleton metal atoms are partly replaced with various metal atom such as Ti, Mn, Co, Fe, Zn, etc., have been developed and widely used.

For better utilization of zeolite or its analogs, studies have been carried out to develop methods of attaching zeolite particles to the surface of substrates such as glass, ceramics, polymeric materials, metal, etc.

The simplest method is to physically attach zeolite particles onto the surface of a substrate by dipping the substrate in a zeolite dispersion (or suspension) in water, followed by taking out and drying the resulting substrate

(L. C. Boudreau, J. A. Kuck, M. Tsapatsis, *J. Membr. Sci.* 1999, 152, 41-59). Since said method depends on a physical attracting force between zeolite and the substrate, the substrate-dipping time in the zeolite dispersion should be very carefully controlled in order to achieve wide and even-spread zeolite particles on the surface of the substrate. In most cases, however, zeolite crystals tend to form a mono-layer on only a part of the surface of substrates, thus it is difficult to obtain a uniform and even monolayer of zeolite particles over the surface of substrate. In addition, since thus prepared zeolite monolayer is present in a state that zeolite particles are adsorbed onto the substrate by mere physical force, the adsorbed zeolite particles can be easily detached from the surface of substrate.

A second method of attaching zeolite particles onto the surface of the substrate is to use a spacer compound which has on its both ends methyldimethoxysilyl group  $\{\text{Me}(\text{MeO})_2\text{Si}-\}$  capable of connecting zeolite to the substrate via covalent chemical bond. This method comprises, firstly, chemically bonding one terminal  $\{\text{Me}(\text{MeO})_2\text{Si}-\}$  group of the spacer compound to surface hydroxyl groups of a  $\text{SnO}_2$  glass substrate, and then, chemically bonding the other terminal  $\{\text{Me}(\text{MeO})_2\text{Si}-\}$  group of the spacer to zeolite (See, Z. Li, C. Lai, T. E. Mallouk, *Inorg. Chem.* 1989, 28, 178-182). Thus prepared zeolite-substrate composite shows a stronger bonding between zeolite and the substrate compared to those obtained from the above-described method, which involves physical adsorption. However, no uniform arrangement of the zeolite particles on the substrate is observed for the method involving a spacer compound. In addition, it is difficult to uniformly attach zeolite particles in a state of a mono-layer according to this method. Further, since both

terminal  $\{\text{Me}(\text{MeO})_2\text{Si}-\}$  groups of the spacer may simultaneously bond to the surface of a substrate to decrease the number of available surface hydroxyl groups, the degree of surface coverage which relates to the surface area of substrate covered with zeolite particles is very low.

The third method of attaching zeolite particles to the substrate comprises chemically bonding zeolite particles to the substrate via an ionic bond in a multi-step process (L. C. Boudreau, J. A. Kuck, M. Tsapatsis, *J. Membr. Sci.* 1999, 152, 41-59). This multi-step process comprises, (i) covalently bonding an aminopropyl group onto the surface of a silicon wafer, (ii) treating the resulting substrate with hydrochloric acid to give a substrate having a cationic ammonium ion, (iii) treating the substrate having cationic charges with poly(styrene-sodium sulfonate) to yield a polymer coating having anionic charges onto the substrate, and (iv) contacting the resulting substrate having a polymer coating with poly(allyl amine), which has been pretreated with hydrochloric acid, to form thereon a polymer coating having cationic charges. After the treatment, the resulting substrate is contacted with zeolite particles having anionic charges on their skeleton to form a zeolite layer over the substrate via an ionic bond. This method has disadvantages of being very complicate and troublesome because more than six treatment steps are required, the distinct arrangement of zeolite particles are not easily obtained (although it has been argued that some extent of arrangement is observed), and the surface coverage is not complete.

Meanwhile, methods are known wherein nuclei of zeolite crystals are generated near the surface of a substrate and they are grown under the hydrothermal preparation conditions of zeolite to form a zeolite film or thin

layer near the surface of a substrate (J. C. Jansen, D. Kashchiev, A. Erdem-Senatalar, *Stud. Surf. Sci. Catal.* 1994, 85, 215-250; R. Althoff, K. Unger, F. Schuff, *Microporous Mater.* 1994, 2, 557-562). However, these methods have disadvantages that the type of substrate is limited to those stable under the hydrothermal preparation conditions and that it is difficult to control the thickness of the zeolite mono-layer or film.

The inventors have extensively studied in order to develop a method of attaching zeolite or its analogs onto various substrates such as materials having surface hydroxyl groups, metals capable of reacting with a thiol group, polymeric materials having reactive functional groups, etc., to prepare a zeolite-substrate composite having a good durability, uniformity and arrangement.

As a result, the inventors have developed a method of conveniently forming a zeolite mono-layer onto a substrate by chemically combining zeolite particles onto the substrate, and a method of conveniently forming a zeolite di- or multi-layer by repeating the above-described zeolite mono-layer formation. In addition, it is also found that thus prepared zeolite mono-layer or multi-layer has a good durability as well as a uniform and regular arrangement, which can give homogeneous and excellent physical and mechanical properties to the zeolite-substrate composite according to the present invention.

#### DISCLOSURE OF INVENTION

The first object of the present invention is to provide a zeolite-substrate composite having a zeolite mono-layer by combining a zeolite

particles onto a substrate in a mono-layer form by using a linking compound via a chemical bond, and preparation thereof.

In the context of the present invention, the term "zeolite" usually means zeolite itself as well as various molecular sieves, especially zeotype molecular sieves and their analogs. Therefore, the term "zeolite" may be replaced with term "molecular sieve (MS)" in the present invention.

In the context of the present invention, the term "chemical bond" means that a functional group is reacted with another functional group such as a surface hydroxyl group, an organic functional group or a metal such as gold, to form any of covalent bond, ionic bond, or coordination bond.

In the context of the present invention, the term "chemically combining" means that a functional group of one material is chemically bonded to a functional group of the other material, in order to connect said two materials through their functional groups.

According to the first object of the present invention, said zeolite-substrate composite having a zeolite mono-layer is of type S-L-Z, S-L<sub>A</sub>-L<sub>B</sub>-Z, S-L<sub>A</sub>-L<sub>S</sub>-L<sub>B</sub>-Z, or the like, wherein S represents a substrate; Z represents zeolite or its analogs; L<sub>A</sub> and L<sub>B</sub> represent a linker derived from linking molecules A and B, respectively, such as an organic compound having at least two terminal functional groups, of which one is capable of chemically bonding to the substrate or zeolite and the other capable of chemically bonding to the substrate, zeolite or to functional groups of other linking compound; L<sub>C</sub> represents a spacer or space linker different from said linker L and capable of chemically bonding to the remaining ending functional groups of linkers A and B.

First embodiment of the present invention relates to a zeolite-substrate composite of type  $S-L_A-L_B-Z$  having a zeolite monolayer chemically bonded to a substrate, which can be prepared by a process comprising the following steps:

(1)  $S-L_A$  linkage formation by chemically combining a linker A to the substrate, wherein one terminal functional group of the linker A is chemical bonded to the surface of the substrate and the resulting  $L_A$  still has the other terminal functional group remained free,

(2)  $Z-L_B$  linkage formation by chemically combining a linker B to zeolite particles, wherein one terminal functional group of the linker B is chemically bonded to the surface of the zeolite particles and  $L_B$  still has the other terminal functional group remained free,

(3)  $S-L_A-L_B-Z$  formation by chemically combining  $S-L_A$  prepared in above step (1) with  $L_B-Z$  prepared in above step (2), wherein said free terminal functional group of linker  $L_A$  in  $S-L_A$  is chemically bonded to said free terminal functional group of the linker  $L_B$  in  $L_B-Z$ .

Second embodiment of the present invention relates to a zeolite-substrate composite of type  $S-L-Z$  having a zeolite mono-layer chemically combined to a substrate, which may be prepared by a process comprising the following steps:

(1)  $S-L$  linkage formation as described above, and

(2)  $S-L-Z$  formation by chemically combining zeolite particles with  $S-L$  prepared in above step (1), wherein said free terminal functional group of linker L in  $S-L$  is chemically bonded to surface hydroxyl groups of the zeolite particles.

In the above embodiments, a  $L-Z$  intermediate composite is firstly



prepared, which is then combined onto the substrate to yield a S-L-Z composite.

Third embodiment of the present invention relates to a zeolite-substrate composite of type S-L<sub>A</sub>-L<sub>C</sub>-L<sub>B</sub>-Z having a zeolite mono-layer chemically bonded onto the substrate, which may be prepared by a process comprising the following steps:

- (1) S-L<sub>A</sub> linkage formation as described above,
- (2) L<sub>B</sub>-Z linkage formation as described above, and

(3) S-L<sub>A</sub>-L<sub>C</sub>-L<sub>B</sub>-Z formation by combining a spacer linking compound with S-L<sub>A</sub> prepared in above step (1) and L<sub>B</sub>-Z prepared in above step (2) in a simultaneous or stepwise manner, wherein the free terminal functional groups of the linker L<sub>A</sub> and the linker L<sub>B</sub> are chemically bonded to a spacer linking compound.

The second object of the present invention is to provide a zeolite multilayer-substrate composite by repeating the process of forming a zeolite monolayer onto the substrate as described above.

According to the second object of the present invention, said zeolite-substrate composite having a zeolite multi-layer can be any type S-(L<sub>A</sub>-L<sub>B</sub>-Z)<sub>n</sub>, S-(L<sub>A</sub>-Z)<sub>n</sub>, S-(L<sub>A</sub>-L<sub>C</sub>-L<sub>B</sub>-Z)<sub>n</sub>, or the combinations of said mono-layer linkage types, for example, S-(L<sub>A</sub>-L<sub>B</sub>-Z)-(L<sub>A</sub>-Z) and S-(L<sub>A</sub>-L<sub>B</sub>-Z)-(L<sub>A</sub>-Z)-(L<sub>A</sub>-L<sub>C</sub>-L<sub>B</sub>-Z), etc., wherein S, Z, L<sub>A</sub> and L<sub>B</sub>, and L<sub>C</sub> represent the same meaning as defined above, and n represents an integer equal to or bigger than 2.

According to one variant of the present invention, the zeolite-substrate composite having a mono-layer or multi-layer of zeolite can be calcined at a high temperature to remove the linking compounds and/or even the substrate.

According to the present invention, it is also possible to control the

thickness of the zeolite-substrate composite by controlling the repetition number of the process described above to form a zeolite multi-layer onto the substrate.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 to 3 are SEM photographs of a zeolite NaA monolayer combined to a glass plate (magnification: x 300, x 2,000 and x 10,000, respectively).

Figure 4 is a SEM photograph of a zeolite NaA monolayer combined to an octadecylsilyl group-stamped glass plate (magnification: x 100).

Figure 5 is a SEM photograph of a zeolite NaA monolayer combined to cellulose substrate (magnification: x 1,800).

Figures 6 and 7 are SEM photographs of a zeolite ZSM-5 monolayer combined to a glass plate (magnification: x 1,000 and x 5,000, respectively).

Figures 8 to 10 are SEM photographs of a zeolite KL monolayer combined to a glass plate (magnification: x 500, x 2,000 and x 3,000, respectively).

Figure 11 is a SEM photograph of a zeolite SAPO-34 monolayer combined to a glass plate (magnification: x 500).

Figure 12 is a SEM photograph of a zeolite NaA monolayer combined to a glass fiber (magnification: x 5,000).

Figures 13 to 15 are SEM photographs of a zeolite ZSM-5 monolayer combined to silica gel, alumina and larger zeolite ZSM-5 (magnification: x 500, x 200 and x 1,500, respectively).

Figure 16 is a SEM photograph of a zeolite NaA monolayer combined to Merrifield resin (magnification: x 1,800).

Figures 17 to 19 are SEM photographs of a double layer of a first zeolite

ZSM-5 layer and a second zeolite NaA layer (Fig 17), a double layer of a first zeolite NaA layer and a second zeolite NaA layer (Fig 18), and a double layer of a first large zeolite ZSM-5 layer and a second zeolite ZSM-5 (smaller than the former ZSM-5) layer (Fig 19) (magnification: x 2,500, x 2,500 and x 1,000, respectively).

Figure 20 is a SEM photograph (magnification: x 4,000) of a zeolite NaA multilayer combined to glass plate by using tetraethoxysilane (TEOS) as a linker molecule.

Figures 21, 23, 25 and 27 are X-ray diffraction (XRD) patterns of conventional powdery zeolite NaA ZSM-5, KL and a molecular sieve SAPO-34, respectively.

Figures 22, 24, 26 and 28 are X-ray diffraction (XRD) patterns of monolayers of zeolite NaA ZSM-5, KL and a molecular sieve SAPO-34 which are prepared and aligned according to the present invention, respectively.

In below, the present invention is further illustrated in detail.

### 1. Type of substrates

Examples of substrate which can be employed in the present invention include:

1) materials containing hydroxyl groups on the surface, selected from a group consisting of:

oxides or mixed oxides of metals and non-metals such as silicon, aluminum, titanium, tin, indium, etc., which can be used alone or in a mixture, for example, quartz, mica,

glass, ITO glass (glass deposited with indium oxide of tin), tin oxide ( $\text{SnO}_2$ ), and other conductive glass,

silica, porous silica, alumina, porous alumina, titanium dioxide, porous titanium dioxide,

silicon wafer and the likes,

2) metals capable of reacting with a thiol group, such as gold, silver, copper, platinum and the like;

3) polymers having various functional groups on their surfaces, such as PVC, a Merrifield peptide resin and the like;

4) semiconductive materials, such as selenium-zinc ( $\text{ZnSe}$ ), gallium-arsenic ( $\text{GaAs}$ ) and indium-phosphor ( $\text{InP}$ ), and the like;

5) synthetic or natural zeolite or molecular sieve analogs, as defined in below; and

6) natural materials of high molecular weight, which carry hydroxyl groups on their surfaces, such as cellulose, starch (amylose and amylopectin), lignin, and the like.

## 2. Type of molecular sieves

Zeolite and its analogs used in the present invention are porous materials having hydroxyl groups on their surface. Specific examples include the following:

1) natural and synthetic zeolite or molecular sieve;

2) modified molecular sieves in which all or a part of the silicon atoms in the zeolite skeleton are replaced with other atoms such as phosphorous (P) or the like (e.g.,  $\text{AlPO}_4$ ,  $\text{SAPO}$ ,  $\text{MeAPO}$ ,  $\text{MeAPSO}$  type molecular sieve);

3) modified molecular sieves in which all or a part of the aluminum atoms in the zeolite skeleton are replaced with other atoms such as boron (B), gallium (Ga), titanium (Ti), etc.;

4) molecular sieves combining the above modifications of item 1) and item 2);

5) porous metals or silicon oxides (e.g.: silicalite, MCM type porous silica, porous titanium dioxide, niobium dioxide, etc.) or mixed oxide thereof; and

6) porous molecular sieves prepared by using any other elements alone or in a mixture.

### 3. Type of linking compounds

In the present invention, substrates and zeolite have on their surface at least one functional group such as hydroxyl group, amino group, or the like. Further, a metal substrate such as gold can react with a compound having a thiol group.

The linking compounds of the present invention is combined with a substrate or zeolite. It is possible to use any compound which has at least two functional groups capable of chemically reacting with surface functional groups of the substrate or zeolite.

The linker, especially the organic linker of the present invention can be derived from linking compounds having at least two terminal functional groups capable of chemically reacting with the surface functional group such as hydroxyl or amino groups of the substrates and/or zeolite via covalent, ionic, or coordination bond, or combination thereof. With a metal substrate such as

gold, it is possible to use a compound having at least one terminal thiol group and at least one terminal functional group other than thiol group.

Therefore, there is no specific restriction to the type of the functional group to be used and a person having an ordinary skill in the art can easily select the type and its combination in an appropriate manner.

One example of the linking compound which can be used in the present invention is an organic compound having at least two terminal functional groups, one being able to react with a hydroxyl group of the substrate or molecular sieve, and the other being able to react with a terminal functional group of other linking compound.

Another example of the linking compound which can be used in the present invention is an organic compound having at least two terminal functional groups, all of which are able to react with the surface hydroxyl group of the substrate or zeolite. For this case, at least one terminal functional group should be remained free without being bonded to the same substrate or zeolite to which any other terminal functional group(s) has/have been bonded, owing to certain sterical and/or conformational arrangement of the functional groups. That is, the free-remained functional group of the linking compound should serve as a linker to a functional group of another linking compound, substrate, or zeolite.

Specifically, examples of such organic compound to form the organic linking chain include the following formulae 1 to 3:



(wherein, Z represents  $-SiR_3$  group or isocyanate group; R independently

represents a halogen atom, a  $C_1\sim C_4$  alkoxy or alkyl group, at least one of three R substituents being halogen or alkoxy group; L represents an organic linking chain or linker selected from divalent hydrocarbon residues such as substituted or unsubstituted  $C_1\sim C_{17}$  alkyl, aralkyl or aryl groups, which may have at least one heteroatom such as oxygen, nitrogen and sulfur; X represents a reactive functional group such as halogen, isocyanate, tosyl, azide, and the like; R' has the same meaning with R, at least two of the four R' substituents being halogen atom or alkoxy group; and M represents Si or a transition metal such as Ti or Zr; and Y represent a ligand having a functional group selected from a group consisting of hydroxyl, thiol, amine, ammonium, sulfone and its salt, carboxylic acid and its salt, acid anhydride, epoxy, aldehyde, ester, acrylate, isocyanate, sugar residues, double bond, triple bond, diene, diyne, alkyl phosphine, alkyl amine and the like, and the functional group can exist in the middle or at the terminal ends of the ligands.

In the present invention, the functional group is selected from a group consisting of halogen, tosyl, azide,  $R_3Si-$  (in which R represents independently a halogen atom,  $C_1\sim C_4$  alkoxy or alkyl group, and at least one of the three R substituents is halogen or alkoxy group), hydroxyl, thiol, amine and its salt, ammonium and its salt, sulfone and its salt, carboxylic acid and its salt, acid anhydride, epoxy, aldehyde, ester, acrylic, isocyanate, sugar residue, double bond, triple bond, diene, diyne, alkyl phosphine, alkyl amine and the like, and the functional group can exist in the middle or at the terminal ends of the ligands.

In the present invention, the linker is selected from a group consisting of divalent  $C_1\sim C_{17}$  alkyl, aralkyl or aryl group, which can be optionally

substituted and contain at least one heteroatom such as oxygen, nitrogen, sulfur or metal atom.

The present invention further encompasses a linking pattern wherein at least two different linkers are chemically bonded and used as a linker.

The reaction of compounds of formulae 1~3 with a substrate or molecular sieve can be carried out by using known chemical methods. However, the composite of <substrate>-<compound of formula 1~3>-<molecular sieve> and preparation thereof has not been reported. Particularly, physical properties and morphological features of the composite thus prepared have not been known.

#### 4. Reaction of substrate or zeolite with linking compounds

Since zeolite has reactive surface hydroxyl groups, it can react with functional groups of the linking compounds. The procedure and conditions of such reaction are well known in the pertinent technical field.

In the context of the present invention, the term "a reactive surface hydroxyl group" of zeolite means a hydroxyl group as well as a hydroxyl-precursor group present on the surface of zeolite. The hydroxyl-precursor group means a group capable of being transformed to a hydroxyl group. Examples of such hydroxyl-precursor group include acyloxy group, methoxy group, or Si=O group. Among these, Si=O group can be easily transformed to a hydroxyl group by hydrolysis.

The linker-zeolite intermediate composite (hereinafter, often referred to as "L-Z or L<sub>B</sub>-Z intermediate composite") can be prepared as follows:

Zeolite and a linking compound are added into an organic solvent. The resulting suspension is heated to prepare L-Z intermediate composite. After



the reaction is completed, the L-Z intermediate composite is taken out and well washed with an organic solvent. In a preferred embodiment, the particles of L-Z intermediate composite can be filtered using a filter paper and then washed. The obtained L-Z intermediate composite particles can be incorporated into toluene and re-dispersed by an ultrasonic washer.

The substrate-linker intermediate composite (herein after, often referred to as "S-L or S-L<sub>A</sub> intermediate composite") can be prepared according to the same procedure described above for the preparation of the L-Z intermediate composite.

Examples of organic solvents include aliphatic hydrocarbons such as hexane, tetrachlorocarbene, alcohols, and aromatic hydrocarbons such as benzene, toluene or xylene. Preferably, toluene is used.

### 5. Linkage types and/or linkage patterns

According to the present invention, the linkage type and/or the linkage pattern can vary depending on the kinds of substrate and zeolite, the type of the functional group of linking compounds and substrates, and/or the order of the reaction.

Typically, the linkage type of the zeolite-linker-substrate composite can be classified into the following three types, type 1, 2 and 3. Based on these three basic types, various linkage patterns can be easily envisaged by a person in this technical field.

#### Type 1: S-L-Z

The linking chain L (or linker L) can be derived from compounds of formula 1 or 2. S-L-A composite can be prepared from zeolite (Z), a linking compound

(L) and a substrate (S) in a stepwise manner or a simultaneous manner.

When a compound of formula 1 is used as a linking compound, the reaction is preferably proceeded in a stepwise manner. A linking compound (L) of formula 1 is firstly reacted with a substrate (S) to prepare a substrate-linker (S-L) intermediate composite, which is then reacted with zeolite particles to prepare a S-L-Z composite, or vice versa. Examples of the linking compound of formula 1 include (3-chloropropyl)trimethoxysilane ( $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ ) and 3-(triethoxysilyl)propyl isocyanate ( $\text{OCNCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3$ ). However, it is also possible to proceed the reaction in a stepwise manner, even if a compound of formula 1 is used.

When a compound of formula 2 is used as a linking compound, the reaction is preferably proceeded in a simultaneous manner. By mixing zeolite, a linking compound of formula 2 and a substrate all together, a S-L-A composite, especially a  $\text{S-MR}'_n\text{-Z}$  composite (wherein, n is an integer of 0 to 4) can be formed. Examples of the compound of formula 2 include tetraethoxysilane (hereinafter, referred to as TEOS) and tetrachlorosilicon ( $\text{SiCl}_4$ ). It is also possible to proceed the reaction in a stepwise manner even if a compound of formula 2 is used.

In a preferred embodiment of the present invention, when fine particles of zeolite are employed as a substrate to form a zeolite layer, a compound of formula 2 is advantageously used as a linking compound.

#### Type 2: $\text{S-L}_A\text{-L}_B\text{-Z}$

The linker  $\text{L}_A$  and  $\text{L}_B$  can be derived from compounds of formula 1 and/or 3. First, a  $\text{S-L}_A$  intermediate composite is prepared by combining a linking compound to a substrate. Separately, a  $\text{L}_B\text{-Z}$  intermediate composite is prepared

by combining a linking compound to zeolite. Then, the resulting S-L<sub>A</sub> intermediate composite and the L<sub>B</sub>-Z intermediate composite are combined to prepare a S-L<sub>A</sub>-L<sub>B</sub>-Z composite. In this case, the linking compounds are selected so that the remaining functional groups of the linkers L<sub>A</sub> and L<sub>B</sub> can get chemically connected to each other.

The reaction between a linker L<sub>A</sub> and a linker L<sub>B</sub> can be carried out by any conventional chemical reaction, including, for example, a substitution reaction (e.g., a reaction between an amino group and a leaving group such as halogen or tosyl group), an ionic bond-formation reaction (e.g., a reaction between an ammonium group and a carboxylic group or its salts), a Diels-Alder reaction (e.g., a reaction between a dien group and an olefin group), a ring-opening reaction (e.g., a reaction between an epoxy group and an amino or hydroxyl group), an amide- or ester-forming reaction, a glycosidic reaction (e.g., glucose, galactose, mannose or the like can be used as a sugar residue), etc.

The type of linker and functional groups, and the reaction type between the free-remained functional group of the linkers may be suitably selected by a person in the pertinent technical field.

### Type 3: S-L<sub>A</sub>-L<sub>C</sub>-L<sub>B</sub>-Z

The linker L<sub>A</sub> and L<sub>B</sub> can be derived from the compounds of formula 1 and/or 3. The linker L<sub>C</sub> is a space linker derived from a space linking compound which is different from L<sub>A</sub> and L<sub>B</sub>.

Said space linker L<sub>C</sub> can be a space linking compound selected from a group consisting of fullerene (C<sub>60</sub>, C<sub>70</sub>), carbon nanotubes, α,ω-dialdehyde, dicarboxylic acid, dicarboxylic acid anhydride, amine-dendrimer,

polyethyleneimine, a , $\omega$ -diamine, a complex of [M(salen)], (M represents a metal element such as Co, Ni, Cr, Mn, Fe and the like, and salen represents *N,N'*-bis(salicyliden)ethylenediamine), metal porphyrine derivatives, and any other coordination compounds.

A S-L<sub>A</sub>-L<sub>C</sub>-L<sub>B</sub>-Z composite can be prepared by simultaneously combining a space linking compound with a S-L<sub>A</sub> intermediate composite and a L<sub>B</sub>-Z intermediate composite. In this case, the linking compounds for the S-L<sub>A</sub> and L<sub>B</sub>-Z intermediate composite are selected so that they have at least one free-remained functional groups capable of reacting with the space linking compound to be used.

The composite S-L<sub>A</sub>-L<sub>C</sub>-L<sub>B</sub>-Z can be prepared by stepwise manner, wherein the S-L<sub>A</sub> intermediate composite is first combined with the spacer linking compound of L<sub>C</sub> to give a S-L<sub>A</sub>-L<sub>C</sub> composite, to which L<sub>B</sub>-Z intermediate composite is then combined to give the S-L<sub>A</sub>-L<sub>C</sub>-L<sub>B</sub>-Z composite, or vice versa.

Examples of combinations of the functional groups of linker L<sub>A</sub> or L<sub>B</sub> with the space linkage compound of L<sub>C</sub> are as follows:

- fullerene or carbon nanotubes .... NH<sub>2</sub>, or N<sub>3</sub> group;
- a , $\omega$ -dialdehyde, dicarboxylic acid, or dicarboxylic acid anhydride .... NH<sub>2</sub> group;
- amine-dendrimer (dendrimer-NH<sub>2</sub>) .... epoxy group, or leaving group such as halogen;
- polyethyleneimine, or diamine .... epoxy group, or leaving group such as halogen.

## 6. Preparation of multilayer

Since zeolite can be used as a substrate according to the present invention, a zeolite mono-layer in a zeolite-substrate composite too can serve as a substrate.

Therefore, it is possible to form another zeolite monolayer on a zeolite-substrate composite to prepare a zeolite layer-zeolite layer-substrate composite, on which a double layer of zeolite is formed over the surface of the substrate. Further, it is also possible to prepare a zeolite multi-layer on a substrate by repeating the above steps for forming a zeolite double-layer.

According to the present invention, the type of zeolite and linkage pattern can be the same or different, depending on the type of each zeolite layer formed in the zeolite multilayer. The linker can be derived from a linking compound of formula 1, 2 or 3, which is described above.

The linkage pattern of a zeolite multi-layer is not specifically limited, but examples thereof can be exemplified as follows:

(6.1) (S-L-Z)-(L-Z)

(linker L and zeolite Z are the same or different),

(6.2) (S-L)-(L-Z-L)-(L-Z)

(linker L and zeolite Z are the same or different),

(6.3) Process using tetraethoxysilane (TEOS)

Drops of distilled water and tetraethoxysilane are added onto the surface of a plain substrate, by using a spin coater resulting a thin layer formed thereon. A dispersion of zeolite is then dropped on the thin layer of water and TEOS. The resulting substrate is rotated to form a thin layer of zeolite particles (that is, an unreacted zeolite monolayer), which is heated to chemically combine the zeolite monolayer to the substrate via a linker

derived from TEOS. By repeating this procedure, a multilayer of zeolite such as double layer, triple layer and so on can be prepared, depending on the number of repetition of the process.

(6.4) Process using [3-(2,3-epoxypropoxy)propyl]trimethoxysilane and a polymer

3-(2,3-Epoxypropoxy)propyl group is firstly bonded to the substrate and then polyethyleneimine is applied. Thereto, particles of zeolite modified with 3-(2,3-epoxypropoxy)propyl group are reacted to prepare a zeolite monolayer on the substrate.

Onto the zeolite monolayer, polyethyleneimine is again applied to form a polymeric layer on the zeolite monolayer, and then zeolite particles modified with 3-(2,3-epoxypropoxy)propyl group are further reacted to form a zeolite double layer on the substrate. By repeating this procedure, a zeolite multilayer can be obtained.

#### (6.5) Calcination

Calcination of a zeolite-linker-substrate composite prepared as above can be carried out in order to remove the organic linker. By doing so, a calcined zeolite-substrate composite, in which zeolite particles are directly combined to substrates and/or to zeolite particles via Si-O-Si bond without being interrupted by organic linking chains, can be obtained.

Thus prepared calcined zeolite-substrate composite has an advantage that it is more durable and/or resistant at high temperature.

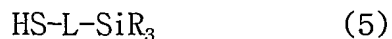
In a preferred embodiment of the present invention, it is clearly understood that a zeolite multi-layer may be further formed onto such calcined zeolite-substrate composite.

### 7. Use of metal substrate

When a metal capable of reacting with a thiol group is employed as a substrate, a compound having at least one terminal thiol group and at least one terminal functional group other than thiol group can be used as a linking compound.

The composite of zeolite and metal can be prepared according to the same or similar method as described before.

Examples of linking compounds having at least one terminal thiol group and at least one terminal functional group other than thiol group are as follows:



wherein, the symbols L, X, R and Y are the same as defined above.

### DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will now be described in detail by following specific but non-limiting embodiments. Figures 1 through 13 attached are referenced together in this connection.

### EXAMPLES

#### Example 1 : Pre-treatment of substrate

A substrate such as glass, silicon wafer or the like was dipped in MN% aqueous hydrochloric acid solution under heating for at least an hour or in a mixed solution of ammonium persulfate and sulfuric acid for at least an 1

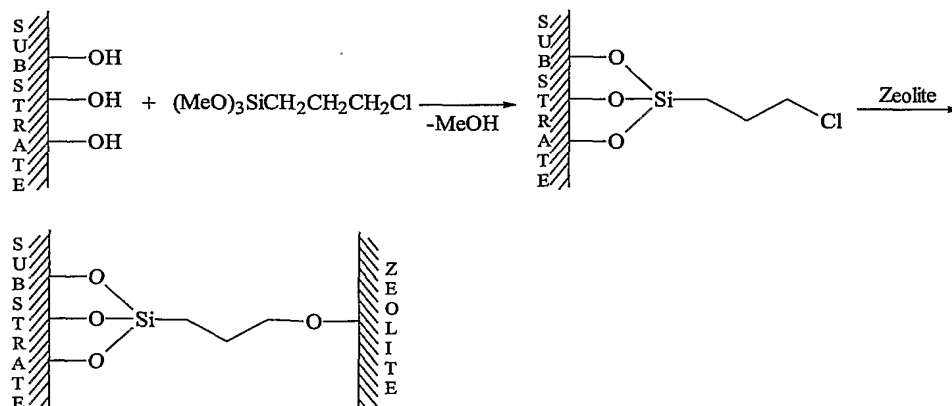
hour. Then, the substrate was washed with distilled water, which was again dipped in an aqueous ammonia solution for about 15 minutes and then in acetic acid for about 30 min. The resulting substrate was thoroughly washed with a distilled water and stored in a distilled water. The substrate was taken and dried when it is to be used.

### Example 2 : Preparation of gold substrate

On a substrate selected from glass, silicon wafer or the like, a metal selected from titanium or chromium was deposited to a thickness of about 100 Å by means of a vacuum heating deposition. When titanium or chromium was used, gold was further deposited to a thickness of about 1000 Å by means of a vacuum heating deposition.

The resulting substrate was washed with piranha solution prepared by mixing sulfuric acid and hydrogen peroxide in a ratio of 7:3. When it is to be used, the substrates was heated at 300 °C under vacuum and cooled.

### Example 3 : Preparation of zeolite monolayer using (3-chloropropyl)trimethoxysilane (CPS)

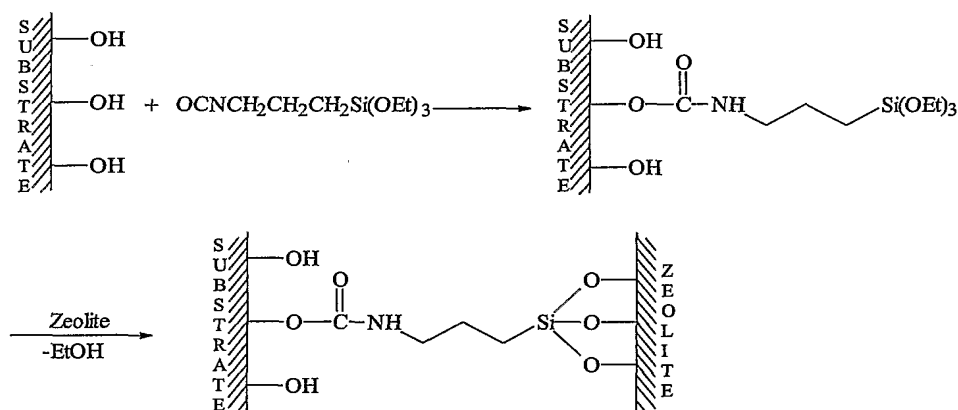




To a reaction vessel containing toluene (30 ml), several glass plates (2 cm x 2 cm) were dipped and (3-chloropropyl)trimethoxysilane (0.5 ml) was added. After being heated for 3 hours, the glass plates were well washed with toluene.

Zeolite particles (0.02 g) were thoroughly dispersed in toluene (30 ml) by using an ultrasonic washer to give a zeolite suspension, in which the glass plates having surface 3-chloropropyl groups obtained above were dipped and subjected to ultrasonic vibration for more than 30 seconds. After being heated for 3 hours and cooled down to room temperature, the glass plate coated with a zeolite monolayer was taken from the suspension, dipped in toluene, and then subjected to an ultrasonic vibration for 1 minute or more to remove any unreacted zeolite particles which were loosely attached on the zeolite monolayer.

Example 4 : Preparation of zeolite monolayer using 3-(triethoxysilyl)propyl isocyanate



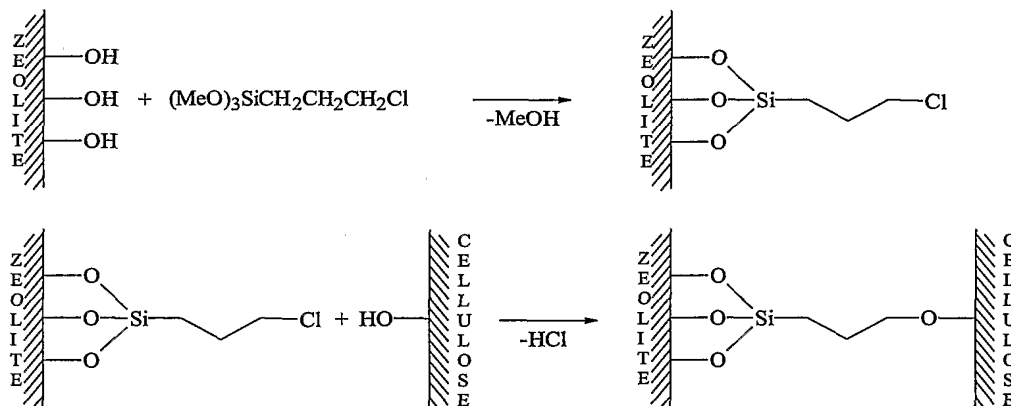
In a reaction vessel containing toluene (30 ml), several glass plates (2 cm x 2 cm) were dipped and 3-(triethoxysilyl)propyl isocyanate was added. While being heated for about 1 hour, silanol groups of the glass reacted with

isocyanate groups to form urethane bonds. The resulting glass plates were then taken out and washed with toluene.

The modified glass plates having surface triethoxysilylpropyl groups were dipped in a zeolite suspension in toluene, and subjected to an ultrasonic vibration for about 30 seconds or more.

After being heated for about 24 hours and cooled down to room temperature, the glass plates coated with a zeolite monolayer were taken out, dipped in toluene, and then subjected to an ultrasonic vibration for about 1 minute or more to remove any unreacted zeolite particles which were loosely attached on the zeolite monolayer.

Example 5 : Preparation of zeolite monolayer on the surface of cellulosic substrate using (3-chloropropyl)trimethoxysilane

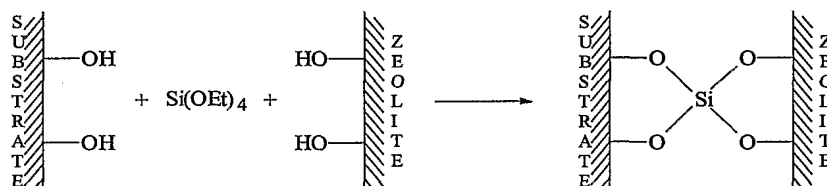


In a reaction vessel containing toluene, zeolite particles were placed and (3-chloropropyl)trimethoxysilane was added. The resulting mixture was heated. After the completion of the reaction, the zeolite particles having surface 3-chloropropyl groups were filtered and washed with an organic solvent such as toluene.

The zeolite particles obtained were well dispersed in toluene by using an ultrasonic washer to give a zeolite suspension, in which a cellulosic material (e.g., filter paper) was dipped and heated for about 3 hours under stirring.

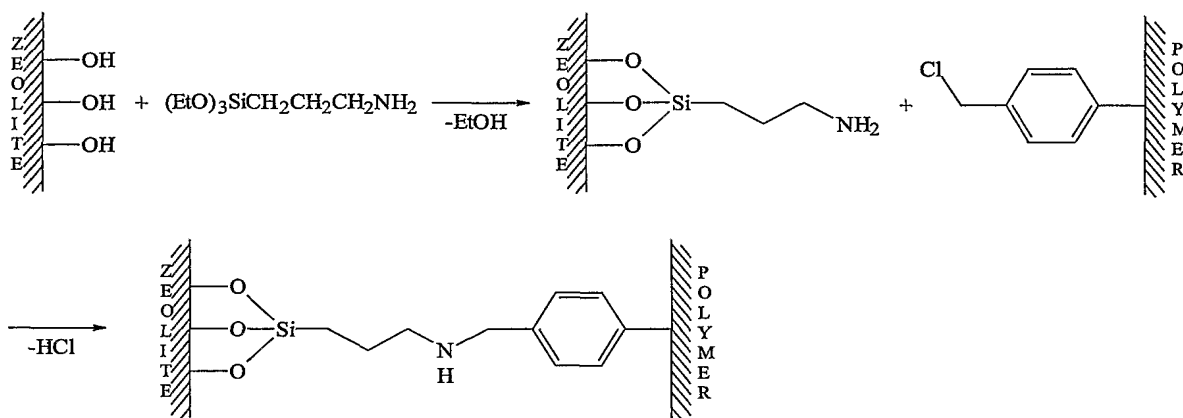
After cooling to room temperature, the resulting cellulosic material having a zeolite monolayer was taken out, dipped in toluene and washed several times with shaking. The modified cellulosic material coated with a zeolite monolayer was subjected to ultrasonic vibration for 30 seconds to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 6 : Preparation of zeolite monolayer using tetraethoxysilane (TEOS)



Zeolite particles containing a small quantity of water were well dispersed in toluene by using an ultrasonic washer. In the resulting suspension, a glass plate well washed was dipped and two or three drops of tetraethoxysilane were added. The resulting mixture was heated for 3 hours at about 120 °C.

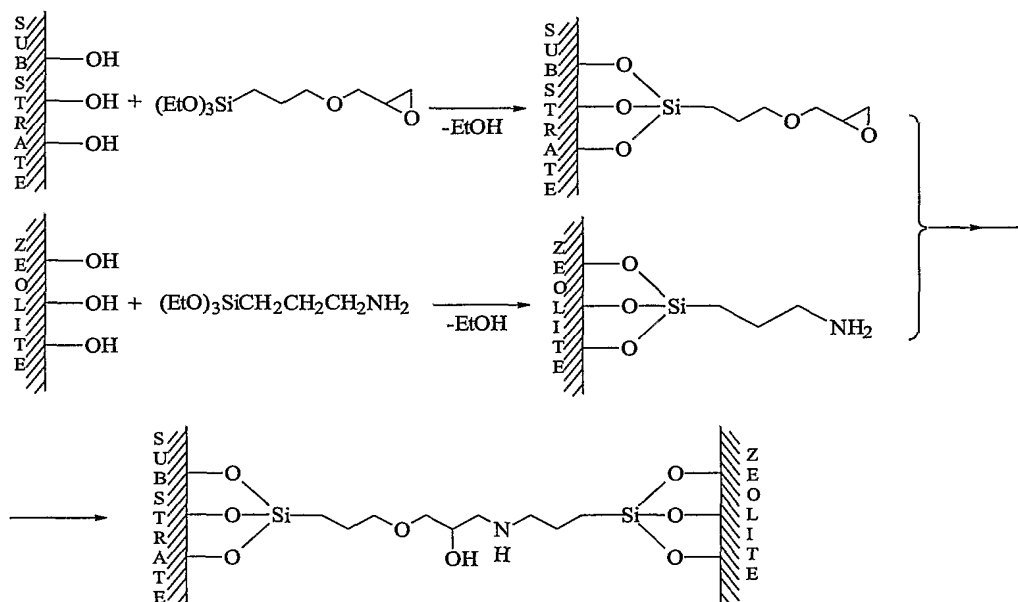
After the reaction, the resulting glass plate coated with a zeolite monolayer was taken out, dipped in toluene, and subjected to a vibration by using an ultrasonic washer for about 20 seconds to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 7 : Preparation of zeolite monolayer on the surface of Merrifield resin

Zeolite particles were placed in a reaction vessel containing toluene and 3-aminopropyltriethoxysilane (APS) was added. The resulting mixture was heated. After the completion of the reaction, the zeolite particles to which 3-aminopropyl groups had bonded were filtered and well washed with an organic solvent.

The zeolite particles obtained were added to a suspension of a Merrifield resin in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and well dispersed by using an ultrasonic washer. The resulting mixture was heated for about 12 hours under stirring. After the reaction, the modified Merrifield resin to which zeolite particles had bonded was removed by filtering it through a filter paper with large pore size and washing it with dichloromethane to remove zeolite particles which were loosely attached on the monolayer.

Example 8: Preparation of zeolite monolayer using EPS and APS

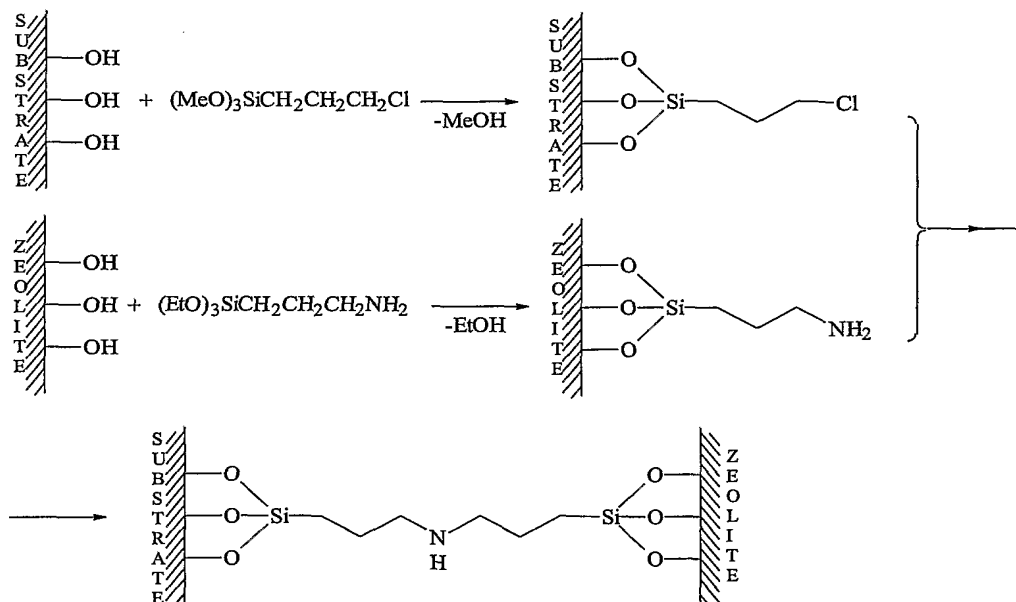


To a solution of [3-(2,3-epoxypropoxy)-propyl]trimethoxysilane (EPS) in toluene, a glass plate was immersed and heated. After the completion of the reaction, the resulting glass plate was taken out and well washed several times with toluene.

To a solution of 3-aminopropylethoxysilane (APS) in toluene, zeolite particles were added and heated. After the completion of the reaction, the resulting zeolite particles were filtered, well washed with toluene, and dispersed in toluene by using an ultrasonic washer to give a suspension.

To the above suspension, the glass plate obtained was dipped and heated for 1 hour or more. After being cooled down to room temperature, the resulting glass plate coated with a zeolite monolayer is taken out, dipped in toluene, and subjected to an ultrasonic vibration to remove any unreacted zeolite particles which were loosely attached on the monolayer.

#### Example 9: Preparation of zeolite monolayer using CPS and APS



A glass plate having surface 3-chloropropyl groups was prepared as described in Example 3 and zeolite particles having surface 3-aminopropyl groups were prepared as described in Example 8.

The zeolite particles having surface 3-aminopropyl groups were dispersed in toluene by using an ultrasonic washer to give a suspension, to which the above-obtained glass plate having surface 3-chloropropyl groups was dipped and heated for at least an hour.

After being cooled down to room temperature, the resulting glass plate coated with a zeolite monolayer thereon was taken out, dipped in toluene, and subjected to an ultrasonic vibration to remove any unreacted zeolite particles which were loosely attached on the monolayer.

#### Example 10: Preparation of zeolite monolayer based on ionic bond

A Glass plate was dipped in a solution containing 3-cyanopropyltrichlorosilane (Cl<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>CN; 0.02 ml) in hexane (50 ml) for 24

hours at room temperature. The resulting glass plate having surface 3-cyanopropyl groups was taken out and dipped in a concentrated hydrochloric acid solution, which was then heated to 95-100 °C for two hours. In doing so, the cyano groups were converted to carboxylic groups by hydrolysis.

The resulting glass plate having surface carboxylic groups [Glass-(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>H] was taken out and dipped in a saturated NaHCO<sub>3</sub> solution for 12 hours. According to this neutralization, protons of the carboxylic acids were replaced with Na<sup>+</sup> ion to give a glass plate having surface carboxylate groups [Glass-(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub><sup>-</sup>Na<sup>+</sup>]. In the same manner, an ion exchange to other cations such as silver ion (Ag<sup>+</sup>), ammonium ion, etc. can be carried out.

Zeolite particles having surface 3-aminopropyl groups were added to a 90% ethanol solution containing NaHCO<sub>3</sub> and iodomethane (CH<sub>3</sub>I) and stirred at 60°C for 24 hours. The resulting zeolite particles having surface -(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>I<sup>-</sup> groups were recovered by filtering them through a filter paper and washing them with ethanol and distilled water.

Zeolite particles having surface -(CH<sub>2</sub>)<sub>3</sub>N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>I<sup>-</sup> groups were well dispersed in ethanol to give a dispersion, in which was dipped a glass plate having various carboxylic acid salts such as -(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub><sup>-</sup>Na<sup>+</sup> groups or -(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub><sup>-</sup>Ag<sup>+</sup> groups on its surface. After increasing the temperature to 60°C to 78°C, the resulting mixture was stood alone for 10 minutes with occasional vibration by using an ultrasonic washer. The resulting glass plate coated with a zeolite monolayer was taken out, dipped in toluene, and subjected to an ultrasonic vibration to remove any unreacted zeolite particles which were loosely attached on the monolayer.

The above procedure according to the present invention has been found

to have advantages such as an excellent surface coverage and simplicity of a process, which are significant improvement compared to the multi-step procedure of Tsapatsis' (L. C. Boudreau, J. A. Kuck, M. Tsapatsis, *J. Membr. Sci.* 1999, 152, 41-59), wherein,  $-(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_3$  ionic groups are first attached to a substrate, and then polymers having surface anionic or cationic groups are adsorbed thereon, and finally zeolite particles having anionic charge on their structural skeleton are attached thereto via an ionic bond.

Example 11 : Preparation of zeolite monolayer using glycoside method

To a solution of  $(\text{MeO})_3\text{Si}-(\text{CH}_2)_{11}-\text{O}-\text{Glu}-\text{OAc}$  in toluene, a glass plate was dipped and heated to  $110^\circ\text{C}$  for about 1 hour under reflux. The resulting glass plate having surface  $-(\text{CH}_2)_{11}-\text{O}-\text{Glu}-\text{OAc}$  groups was taken out and dried, then dipped in a solution containing a catalytic amount of sodium hydroxide in methanol at  $0^\circ\text{C}$  for 12 hours to give a glass plate having surface  $-(\text{CH}_2)_{11}-\text{O}-\text{Glu}-\text{OH}$  groups.

To a solution of  $(\text{MeO})_3\text{Si}-(\text{CH}_2)_{10}-\text{CO}-\text{Glu}-\text{OAc}$  in toluene, zeolite particles were added and heated to  $110^\circ\text{C}$  for 1 hour under reflux. The resulting zeolite particles having surface  $(\text{CH}_2)_{11}-\text{O}-\text{Glu}-\text{OAc}$  groups were recovered by filtering them through a filter paper.

The above-obtained zeolite particles having surface  $(\text{CH}_2)_{10}-\text{CO}-\text{Glu}-\text{OAc}$  groups were dispersed well in toluene, to which the above-obtained glass plate having surface  $(\text{CH}_2)_{11}-\text{O}-\text{Glu}-\text{OH}$  groups was dipped and heated to  $110^\circ\text{C}$  and refluxed for 4 hours. The resulting glass plate coated with a zeolite monolayer was taken out, dipped in toluene, and then subjected to an ultrasonic vibration to remove any unreacted zeolite particles which were loosely attached on the



monolayer.

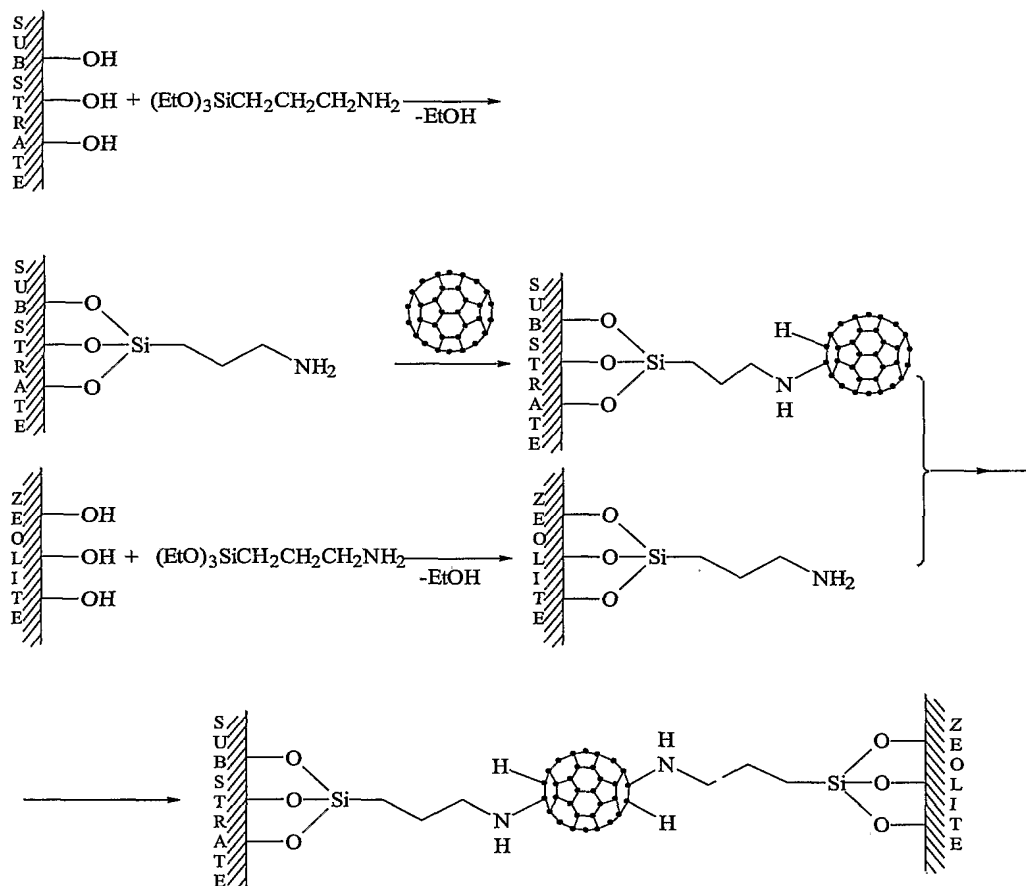
Example 12 : Preparation of zeolite monolayer based on Diels-Alder reaction

To a solution of [3-(2-cyclopentadienyl)propyl]trimethoxysilane in toluene, a glass plate was dipped and heated for 2 hours, and then taken out and washed well several times with toluene.

Zeolite particles were washed with distilled water, dried, and then added to a solution of trimethoxy(7-octen-1-yl)silane in toluene and heated for about 2 hours. By doing so, (7-octen-1-yl)silyl groups were covalently attached to the surface of the zeolite particles to give zeolite particles having surface (7-octen-1-yl)silyl groups.

The above-obtained glass plate was dipped in the above toluene solution containing zeolite particles having surface (7-octen-1-yl)silyl groups and heated for about two hours. The resulting opaque glass plate coated with a zeolite monolayer was taken out and subjected to an ultrasonic vibration in toluene to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 13 : Preparation of zeolite monolayer using fullerene (C<sub>60</sub>)



A glass plate was dried at 120°C for 3 hours, exposed on a vapor of 3-aminopropyltriethoxysilane (APS) to proceed a reaction at 100°C for 15 minutes, washed with ethanol and distilled water, and cured at 120°C. The resulting glass plate having surface 3-aminopropyl groups and fullerene were added into toluene and heated for 5 to 24 hours in order to chemically bond the fullerene to the glass plate.

Zeolite particles (50 mg) were thoroughly washed with distilled water, dried, and then added to a solution of APS (0.3 ml) in toluene (10 ml) and heated for 1 hour. The resulting zeolite particles having surface 3-aminopropyl groups were filtered, washed with toluene and ethanol, and cured at 120°C for 30 min.

The above-obtained glass plate and zeolite particles are added into toluene (20 ml) and heated for more than 5 hours. The resulting glass plate coated with a zeolite monolayer was taken out, washed with toluene, and subjected to an ultrasonic vibration for more than 10 sec to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 14: Preparation of zeolite monolayer using  $\alpha,\omega$ -dialdehyde

A glass plate was dipped in a solution of 3-aminopropyltriethoxysilane (APS) in toluene and heated under reflux at 120°C for 3 hours. Zeolite particles were added to a solution of 3-aminopropyltriethoxysilane (APS) in toluene and heated under reflux for 3 hours.

The above-obtained glass plate having surface 3-aminopropyl groups and zeolite particles having surface 3-aminopropyl groups are added to a solution of terephthalaldicarboxaldehyde ( $\text{OHC-C}_6\text{H}_4\text{-CHO}$ ) in toluene containing a catalytic amount of acetic acid, and heated under reflux at 110 °C for 3 hours. After cooling, the resulting glass plate was taken out, dipped in toluene, and subjected to an ultrasonic vibration in toluene to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 15: Preparation of zeolite monolayer using amine-dendrimer

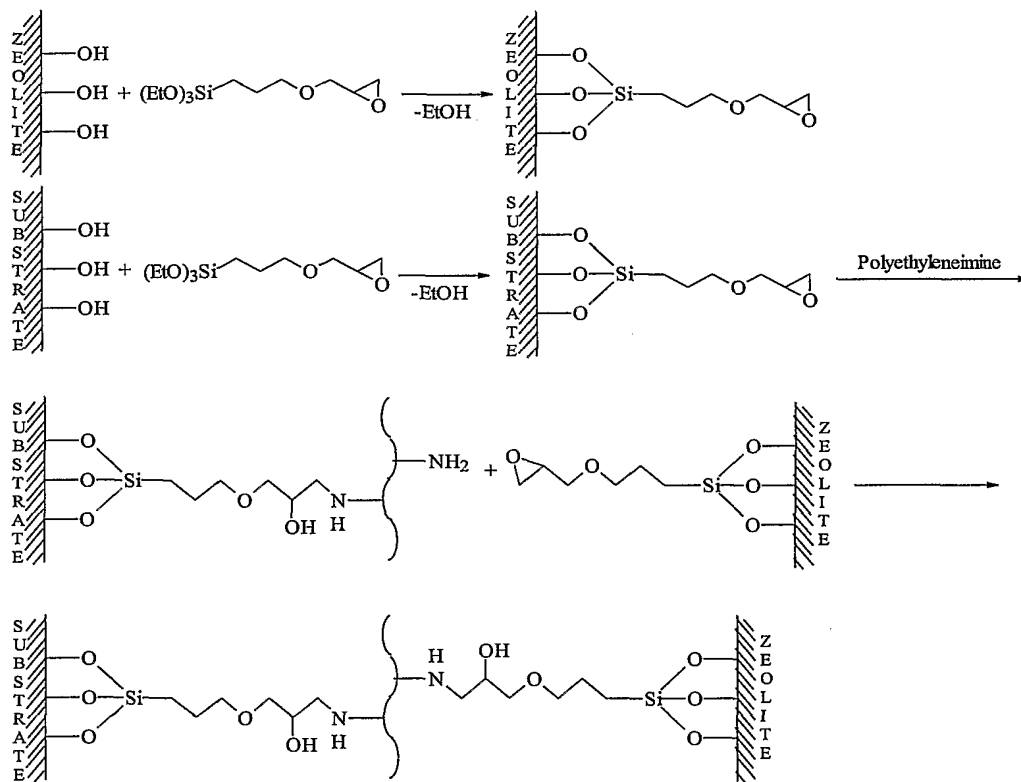
A glass plate was dipped in a solution of [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (EPS) in toluene and heated for 2 hours. The resulting glass plate was taken out, well washed with toluene several times, dipped in a solution of a dendrimer (0.03 ml) in methanol (20 ml), and heated for 2 hours. After being then taken out, the plate was well washed with methanol

and distilled water, then dried.

Zeolite particles were washed with distilled water, dried, and then added to a solution of [3-(2,3-epoxypropoxy)propyl]trimethoxysilane in toluene and heated for 2 hours to give zeolite particles having surface 3-(2,3-epoxypropoxy)propyl groups.

The above-obtained glass plate and zeolite particles were added into toluene and heated for 8 hours. After cooling, the resulting opaque glass plate coated with a zeolite monolayer was taken out, dried at 120 °C for 1 hour, and subjected to an ultrasonic vibration in toluene for more than 10 sec to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 16: Preparation of zeolite monolayer using polyethyleneimine



A glass plate was dipped in a solution of [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (EPS; 2 mM) in toluene (10 ml) and heated for 1 hour. The resulting glass plate was taken out, well washed with toluene several times, dipped in a solution of a low molecular weight polyethyleneimine (40 mg) in toluene, and heated for 1 hour. Unbound polymer was washed and removed by heating for 1 hour in toluene and then for 1 hour in dichloromethane. The resulting glass plate was well washed with toluene several times.

Zeolite particles (0.2 g) were washed with distilled water, dried, and then added to a solution of [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (2 mM) in toluene (10 ml) and heated for 1 hour to give zeolite particles having surface 3-(2,3-epoxypropoxy)propyl groups linked via covalent bond.

The above-obtained glass plate was dipped in the toluene solution containing zeolite particles (0.1 g) having surface 3-(2,3-epoxypropoxy)propyl groups and heated for two hours. The resulting opaque glass plate coated with a zeolite monolayer was taken out and subjected to an ultrasonic vibration in toluene for more than 30 sec to remove any unreacted zeolite particles which were loosely attached on the monolayer.

#### Example 17: Preparation of zeolite monolayer using 4,4'-bipyridine

A glass plate having surface 3-chloropropyl groups and zeolite particles having surface 3-chloropropyl groups were prepared by reacting them with (3-chloropropyl)trimethoxysilane (CPS) in toluene.

To a toluene solution containing a small amount of 4,4'-bipyridine, the above-obtained glass plate and zeolite particles were added and heated.

After being cooled down to room temperature, the resulting glass plate

coated with a zeolite monolayer was taken out, dipped in toluene and subjected to an ultrasonic vibration in toluene for more than 30 sec to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 18: Preparation of zeolite monolayer using [Co(salen)] complex

A glass plate having surface 3-aminopropyl groups and zeolite particles having surface 3-aminopropyl groups were prepared by reacting them with 3-aminopropyltriethoxysilane (APS) in toluene, respectively.

To a mixed solution of ethanol and toluene containing [Co(salen)] complex, the above-obtained zeolite particles having surface 3-aminopropyl groups were added and heated. As a result, the amino groups attached to zeolite particles became to get coordinated with [Co(salen)].

The resulting zeolite particles were well dispersed in toluene, in which the above-obtained glass plate having surface 3-aminopropyl groups was dipped and heated for more than 1 hour.

After the completion of the reaction, the resulting glass plate was taken out, dipped in toluene and subjected to an ultrasonic vibration in toluene for more than 30 sec to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 19: Preparation of zeolite monolayer using (3-chloropropyl)trimethoxysilane

A glass plate coated with a zeolite monolayer was prepared according to the same procedure as described in Example 3. Separately, a suspension of zeolite particles having surface 3-chloropropyl groups were prepared and well

dispersed in toluene to prepare a suspension, in which the above-obtained glass plate was dipped and heated to form a zeolite double-layer on the surface of the glass plate.

After the completion of the reaction, the resulting glass plate was taken out, dipped in toluene and subjected to an ultrasonic vibration in toluene for more than 30 sec to remove any physically adsorbed zeolite particles, to obtain a glass plate coated with a zeolite double-layer.

Example 20: Preparation of zeolite double-layer using CPS and APS

A glass plate coated with a zeolite monolayer was prepared according to the same procedure as described in Example 9. Separately, a suspension of zeolite particles having surface 3-chloropropyl groups were prepared and well dispersed in toluene to prepare a suspension, in which the above-obtained glass plate was dipped and heated to form a zeolite double-layer on the surface of the glass plate.

Example 21: Preparation of zeolite multilayer using tetraethoxysilane

A glass plate well washed was mounted on a spin coater. Two or three drops of distilled water were dropped on the glass plate, which was then rotated to remove excess water and thus to obtain a thin water film on the surface of the plate.

One or two drops of tetraethoxysilane were dropped on the above glass plate, which was then rotated to form a thin tetraethoxysilane film over the thin water film. The resulting plate was slightly heated to induce the reaction between water and tetraethoxysilane.

One or two drops of a zeolite suspension was dropped on the resulting glass plate, which was then rotated to form a thin film of zeolite suspension and slightly heated to combine zeolite particles to the glass plate.

By repeating the above procedure, a zeolite multi-layer could be formed on the surface of the glass plate.

Example 22: Preparation of zeolite multilayer using EPS and a polymer

To a glass plate, [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (EPS) in toluene was applied and polyethyleneimine was combined thereto by heating. The resulting glass plate was heated in toluene for 30 min in three times to remove unreacted polymer.

To the resulting glass plate, zeolite particles having surface 3-(2,3-epoxypropoxy)propyl groups are introduced to form a zeolite monolayer, which was then subjected to an ultrasonic vibration to remove any unreacted zeolite particles which was loosely attached on the monolayer.

On the above-obtained zeolite monolayer, polyethyleneimine was added and heated for 1 hour to form a polymer layer, then zeolite particles having surface 3-(2,3-epoxypropoxy)propyl groups were again reacted to form a second layer of zeolite. By doing so, a zeolite double-layer was formed.

By repeating the above steps, that is, the polymer-layer forming step and the zeolite-layer forming step, a zeolite multilayer could be formed on the surface of the glass plate.

Example 23: Preparation of zeolite monolayer on a gold plate using 3-chloro-1-propanethiol (CPT)



A gold plate prepared as in Example 2 was dipped for 24 hours in a solution of 3-chloro-1-propanethiol (2 mM) in ethanol and then taken out and washed with ethanol.

The above-obtained gold plate having surface 3-chloropropyl groups was dipped in a zeolite suspension in toluene and stood for 48 hours or heated for 24 hours.

After being cooled down to room temperature, the resulting gold plate coated with a zeolite monolayer was taken out and subjected to an ultrasonic vibration in toluene to remove any unreacted zeolite which were loosely attached on the monolayer.

Example 24: Preparation of zeolite monolayer on a gold plate using 3-mercaptopropyltrimethoxysilane (MPS)

Zeolite particles were well dispersed in toluene by using a ultrasonic washer, to which 3-mercaptopropyltrimethoxysilane was added and heated for 1 hour. After being cooled down to room temperature, the resulting zeolite particles were filtered, well washed with toluene and ethanol, and dried at 120 °C for 30 min.

The above-obtained zeolite particles having surface 3-mercaptopropyl group were well dispersed in toluene or ethanol by using a ultrasonic washer, to which a gold plate prepared as in Example 2 was dipped and heated at 80 °C for 24 hours.

After being cooled down to room temperature, the resulting gold plate coated with a zeolite monolayer was taken out and subjected to an ultrasonic vibration in toluene to remove any unreacted zeolite particles which were

loosely attached on the monolayer.

Example 25: Preparation of zeolite monolayer on a gold plate based on amide bond

A gold plate prepared as in Example 2 was dipped for 24 hours in a solution of 11-mercaptoundecanoic acid (MUA) (2 mM) in ethanol and then taken out and washed with ethanol.

Zeolite particles were well dispersed in toluene by using an ultrasonic washer, to which 3-aminopropyltriethoxysilane (APS) was added and heated for 1 hour.

After being cooled down to room temperature, the resulting zeolite particles were filtered, well washed with toluene and ethanol, and dried at 120 °C for 30 min.

(i) Using diisopropylamine (DIC):

The gold plate modified with MUA, the zeolite particles having surface 3-aminopropyl groups, 4-dimethylaminopyridine (DMAP) and diisopropylamine were added all together to toluene and heated at 80°C for 48 hours.

After cooling to room temperature, the resulting gold plate coated with a zeolite monolayer was taken out and subjected to an ultrasonic vibration in toluene to remove any unreacted zeolite particles which were loosely attached on the monolayer.

(ii) Using an anhydride:

The gold plate modified with MUA was dipped for 20 min in a solution of 0.2 M triethylamine in anhydrous dimethylformamide (DMF) and washed with dichloromethane. The resulting gold plate was dipped in toluene and reacted

with the above-obtained zeolite particles having surface 3-aminopropyl groups for 48 hours.

After cooling to room temperature, the resulting gold plate coated with a zeolite monolayer was taken out and subjected to an ultrasonic vibration in toluene to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 26: Preparation of zeolite monolayer on gold plate using CPT and APS

A gold plate prepared as in Example 2 was dipped for 24 hours in a solution of 3-chloro-1-propanethiol (2 mM) in ethanol and then taken out and washed with ethanol.

Zeolite particles having surface 3-aminopropyl groups were prepared as in Example 25, were well dispersed in toluene by using an ultrasonic washer, to which the above-obtained gold plate having surface 3-chloropropyl groups was dipped and stood for 48 hours or heated for 24 hours.

After cooling to room temperature, the resulting gold plate coated with a zeolite monolayer was taken out and subjected to an ultrasonic vibration in toluene to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 27: Preparation of zeolite monolayer on gold plate using 2-aminoethanethiol (AET) and EPS

A gold plate prepared as in Example 2 was dipped for 24 hours in a solution of 2-aminoethanethiol (2 mM) in ethanol and then taken out and washed with ethanol.

Zeolite particles were well dispersed in toluene by using an ultrasonic washer, to which [3-(2,3-epoxypropoxy)propyl]trimethoxysilane was added and heated for 1 hour. After being cooled down to room temperature, the resulting zeolite particles were filtered, well washed with toluene and ethanol, and dried at 120 °C for 30 min.

The resulting zeolite particles were well dispersed in toluene by using an ultrasonic washer, to which the above-obtained gold plate having surface amino groups was dipped and stood at room temperature for 48 hours or heated for 24 hours.

After being cooled down to room temperature, the resulting gold plate coated with a zeolite monolayer was taken out and subjected to an ultrasonic vibration in toluene to remove any unreacted zeolite particles which were loosely attached on the monolayer.

Example 28: Preparation of zeolite monolayer on gold plate using polyethyleneimine

A gold plate prepared as in Example 2 was dipped for 24 hours in a solution of 11-mercaptoundecanoic acid (MUA) (2 mM) in ethanol and then taken out and washed with ethanol.

Zeolite particles having surface 3-(2,3-epoxypropoxy)propyl groups were prepared as in Example 27.

After the gold plate modified with MUA was dipped for 20 min in a solution of 0.1 M trifluoroacetic anhydride and 0.2 M triethylamine in anhydrous dimethylformamide, the resulting gold plate was taken out, washed with dichloromethane, and dipped for 30 min in isopropyl alcohol containing 1%

polyethyleneimine, and then taken out and washed with ethanol and water.

To the resulting glass plate, zeolite particles having surface 3-(2,3-epoxypropoxy)propyl groups are applied to form a zeolite monolayer thereon. The plate was subjected to an ultrasonic vibration to remove any unreacted zeolite particles which were loosely attached on the monolayer.

#### Example 29: Scanning Electron Microscope (SEM) Analysis

A platinum/palladium coating with a thickness of about 15 nm was applied on the zeolite monolayer or multilayer composites prepared as in the above Examples, which were then subjected to a SEM analysis by a differential scanning electronic microscope (Hitachi S-4300). Figures 1 to 20 are SEM photos of the composites prepared according to the Examples of the present invention.

#### Example 30: X-ray powder diffraction (XRD) analysis

X-ray powder diffraction patterns are obtained by using a Rigaku X-ray diffraction (CuK $\alpha$  X-ray) from zeolites prepared according to the present invention.

Figures 21, 23, 25 and 27 are XRD patterns obtained from powdery zeolite or its analog which are not arranged, and Figures 22, 24, 26 and 28 are XRD patterns obtained from zeolites or its analog which are prepared and arranged according to the present invention.

#### Industrial Applicability

According to the present invention, a zeolite monolayer or multilayer can be formed on the surface of various substrates via chemical bond. The

zeolite-substrate composite prepared by the present invention is durable and the attached zeolite particles have a highly oriented arrangement. The thickness of zeolite layer and the repeating number of zeolite layers can be conveniently controlled.

The zeolite monolayer and multilayer prepared according to the present invention can be advantageously used in the fields of related to a separation of gas or liquid, a linear or nonlinear optical device, opto-electronics, membrane, membrane catalyst, sensor carrier, photocell, a film formation using a second growth of zeolite, etc.

What is claimed is :

1. A zeolite-substrate composite constituted by a zeolite monolayer or multilayer which is bound on the surface of substrate comprising:

(i) a substrate selected from a group consisting of a substrate having surface hydroxyl groups, a metal substrate capable of being reacted with thiol groups, and a polymeric substrate having reactive functional groups in the main chain or side chains,

(ii) molecular sieve particles selected from porous oxides or sulfides having surface hydroxyl groups,

(iii) a linker derived from a linking compound having at least two functional groups at both terminal ends, of which one terminal end is chemically bonded to said substrate and the other is chemically bonded to said zeolite,

wherein the chemical bonding of said linker to the substrate and to the zeolite or its analog is attained by covalent bonds, ionic bonds, and/or coordination bond,

wherein said linker is a linking chain or a combination of linking chains derived from one or more organic linking compounds selected from a group consisting of the following compounds of formulae 1 to 6:



wherein, Z represents  $-\text{SiR}_3$  group or isocyanate group; R independently represents a halogen atom, a  $\text{C}_1\text{--}\text{C}_4$  alkoxy or alkyl group, at least one of three R substituents being halogen or alkoxy group; L represents an organic linking chain or linker selected from divalent hydrocarbon residues such as substituted or unsubstituted  $\text{C}_1\text{--}\text{C}_{17}$  alkyl, aralkyl or aryl groups, which may have at least one heteroatom such as oxygen, nitrogen and sulfur; X represents a reactive functional group such as halogen, isocyanate, tosyl, azide, and the like; R' has the same meaning with R, at least two of the four R' substituents being halogen atom or alkoxy group; M represents Si or a transition metal such as Ti or Zr; and Y represent a ligand having a functional group selected from a group consisting of hydroxyl, thiol, amine, ammonium, sulfone and its salt, carboxylic acid and its salt, acid anhydride, epoxy, aldehyde, ester, acrylate, isocyanate, sugar residues, double bond, triple bond, diene, diyne, alkyl phosphine, alkyl amine and the like, and the functional group can exist in the middle or at the terminal ends of the ligands.

2. The zeolite-substrate composite according to claim 1, characterized in that said substrate is selected from a group consisting of:

- 1) an oxides or mixed oxides of metals and non-metals having surface hydroxyl groups;
- 2) metals capable of reacting with a thiol group;
- 3) polymers having various functional groups on their surface;
- 4) semiconductive materials;
- 5) synthetic or natural zeolite or its analogs; or
- 6) natural materials of high molecular weight, which carry hydroxyl



groups on their surfaces,

or said zeolite or its analog is selected from a group consisting of:

- 1) natural or synthetic zeolite;
- 2) modified molecular sieves in which all or a part of the silicon atoms in the zeolite skeleton are replaced with other atoms;
- 3) modified molecular sieve in which all or a part of the aluminum atoms in the zeolite skeleton are replaced with other atoms;
- 4) molecular sieves combining the above modifications 2) and 3);
- 5) porous metals or silicon oxides or mixed oxides thereof;
- 6) porous molecular sieves prepared by using any other elements alone or in a mixture.

3. The zeolite-substrate composite according to claim 2, characterized in that said substrate is selected from a group consisting of:

- 1) an oxide or mixed oxide of metals and non-metals such as silicon, aluminum, titanium, tin or indium, selected from a group consisting of a group comprising quartz, mica, glass, ITO glass, various conductible glass such as tin oxide ( $\text{SnO}_2$ ), silica, porous silica, alumina, porous alumina, titanium dioxide, porous titanium dioxide or silicon wafer;
- 2) a metal such as gold, silver, copper or platinum;
- 3) a polymer having various functional groups on its surface, such as PVC or a Merrifield peptide resin;
- 4) a semiconductive material such as selenium-zinc (ZnSe), gallium-arsenic (GaAs) and indium-phosphor (InP), and the like;
- 5) zeolite or molecular sieve analogs, as defined in below;

6) natural materials of high molecular weight which carry hydroxyl groups on the surface, such as cellulose, starch (amylose and amylopectin), lignin, and the like;

or said zeolite or its analog is selected from a group consisting of:

1) natural or synthetic zeolite;

2) modified molecular sieves in which all or a part of the silicon atoms in the zeolite skeleton are replaced with other atoms, selected from a group consisting of  $\text{AlPO}_4$  type, SAPO type, MeAPO type or MeAPSO type molecular sieve or its analogs;

3) modified molecular sieve in which all or a part of the aluminum atoms in the zeolite skeleton are replaced with other atoms selected from a group consisting of boron (B), gallium (Ga) or titanium (Ti) ;

4) molecular sieves combining the above modifications 2) and 3);

5) porous metal or silicon oxides or mixed oxides thereof selected from a group consisting of silicalite, MCM type porous silica, porous titanium dioxide or niobium dioxide;

6) porous molecular sieves prepared by using any other elements alone or in a mixture.

4. The zeolite-substrate composite according to any one of claims 1 to 3, characterized in that said linker comprises in its chain a space linker derived from a space linking compound selected from a group consisting of fullerene ( $\text{C}_{60}$ ,  $\text{C}_{70}$ ), carbon nanotubes,  $\alpha$ ,  $\omega$ -dialdehyde, dicarboxylic acid, dicarboxylic acid anhydride, amine-dendrimer, polyethyleneimine,  $\alpha$ ,  $\omega$ -diamine, a complex of  $[\text{M}(\text{salen})]$  (wherein, M represents a metal element such

as Co, Ni, Cr, Mn or Fe, and salen represents *N,N'*-bis(salicyliden)ethylenediamine), metal porphyrine derivatives, and any other coordination compounds.

5. A Method for the preparation of a zeolite-substrate composite having a zeolite monolayer or multilayer bound on the surface of the substrate according to any one of claims 1 to 3, which comprises:

(i) chemically combining a substrate (S) or zeolite or its analog (Z) with a linking compound ( $L_A$ ) having at least two terminal functional groups to prepare a substrate-linker ( $S-L_A$ ) intermediate composite or a linker-zeolite ( $L_B-Z$ ) intermediate composite,

(ii) chemically combining said intermediate composites with zeolite or its analog (Z) or a substrate (S) to prepare a substrate-linker-zeolite ( $S-L-Z$ ) composite, and

(iii) optionally calcining the resulted composite.

6. A Method for the preparation of a zeolite-substrate composite having a zeolite monolayer or multilayer bound on the surface of the substrate according to any one of claims 1 to 3, which comprises:

(i) mixing substrate (S), zeolite or its analog (Z), and a linking compound (L) having at least two terminal functional groups,

(ii) chemically combining them in a simultaneous manner to prepare a substrate-linker-zeolite ( $S-L-Z$ ) composite, and

(iii) optionally calcining the resulted composite.

7. A Method for the preparation of a zeolite-substrate composite having a zeolite monolayer or multilayer bound on the surface of the substrate according to any one of claims 1 to 3, which comprises:

(i) chemically combining a substrate (S) with a linking compound ( $L_A$ ) having at least two terminal functional groups to prepare a substrate-linker ( $S-L_A$ ) intermediate composite,

(ii) chemically combining zeolite or its analog (Z) with a linking compound ( $L_B$ ) having at least two terminal functional groups to prepare a linker-zeolite ( $L_B-Z$ ) intermediate composite,

(iii) chemically combining said a substrate-linker ( $S-L_A$ ) intermediate composite and said a linker-zeolite ( $L_B-Z$ ) intermediate composite in the presence or absence of a space linker ( $L_S$ ), and

(iv) optionally calcining the resulted composite.

8. The Method according to claim 7, characterized in that said space linker ( $L_S$ ) is derived from a space linking compound selected from a group consisting of fullerene ( $C_{60}$ ,  $C_{70}$ ), carbon nanotubes,  $\alpha, \omega$ -dialdehyde, dicarboxylic acid, dicarboxylic acid anhydride, amine-dendrimer, polyethyleneimine,  $\alpha, \omega$ -diamine, a complex of  $[M(\text{salen})]$  (wherein, M represents a metal element such as Co, Ni, Cr, Mn or Fe, and salen represents *N,N'*-bis(salicyliden)ethylenediamine), metal porphyrine derivatives, and any other coordination compounds.

9. A method of preparing a zeolite-substrate composite having a zeolite multilayer defined in any one of claims 1 to 3, by repeating the method defined

in any one of claims 5 to 8 or a combination thereof.

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FIGURE 1

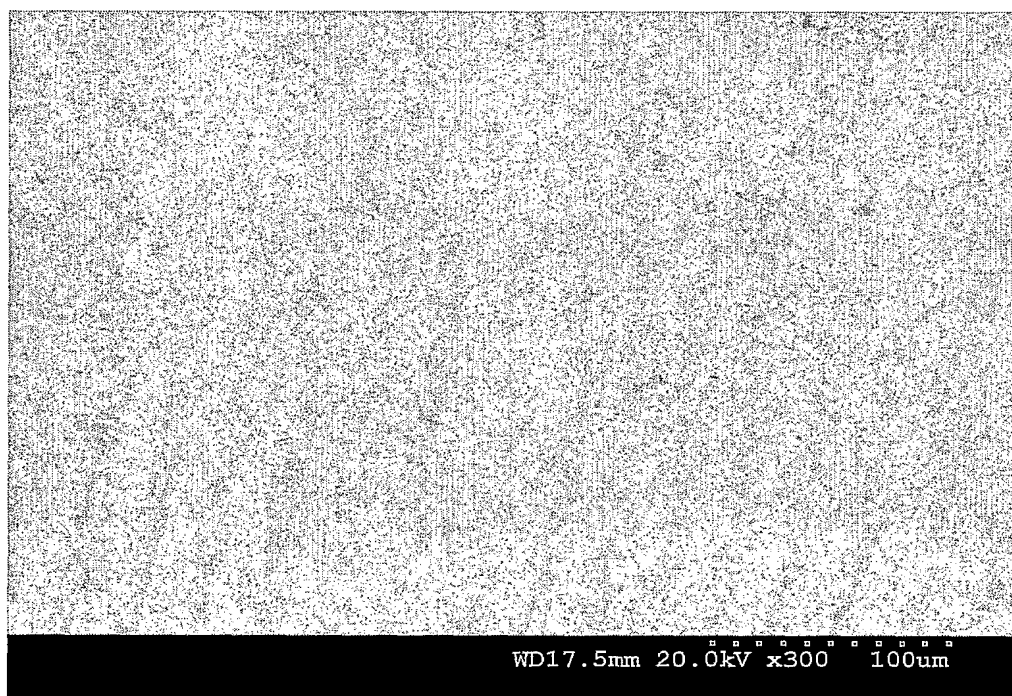
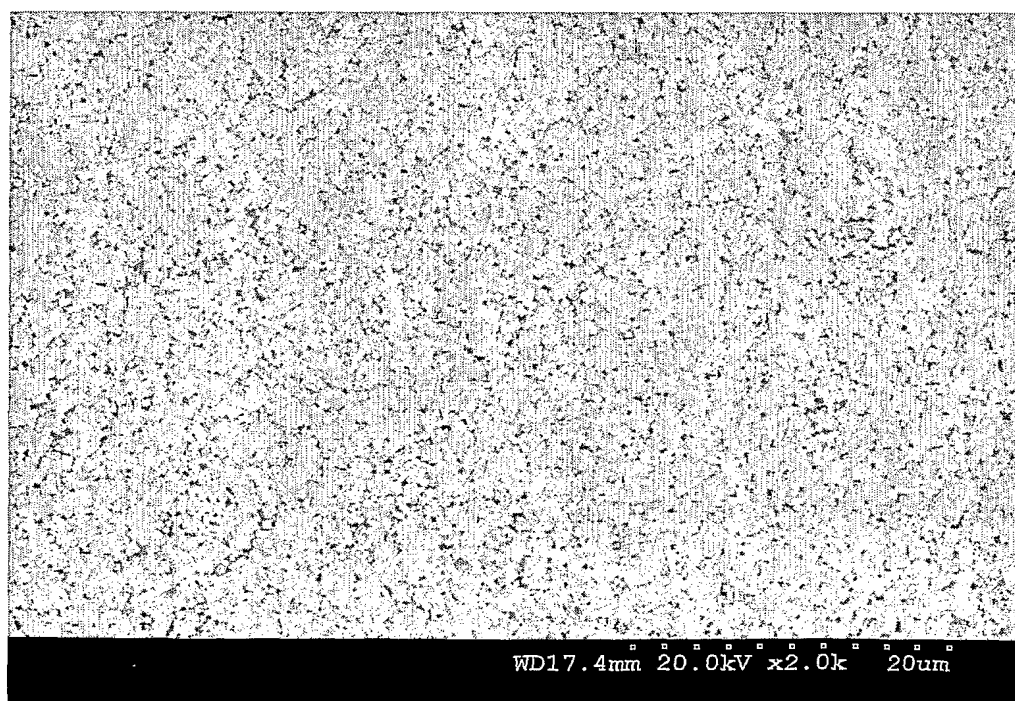


FIGURE 2



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FIGURE 3

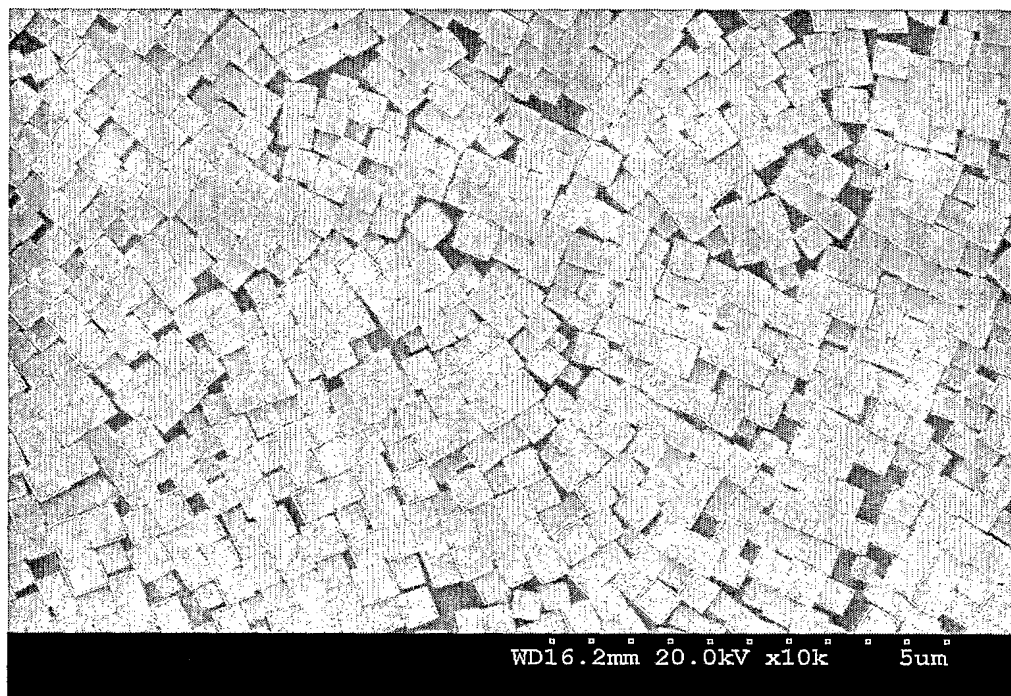


FIGURE 4



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FIGURE 5

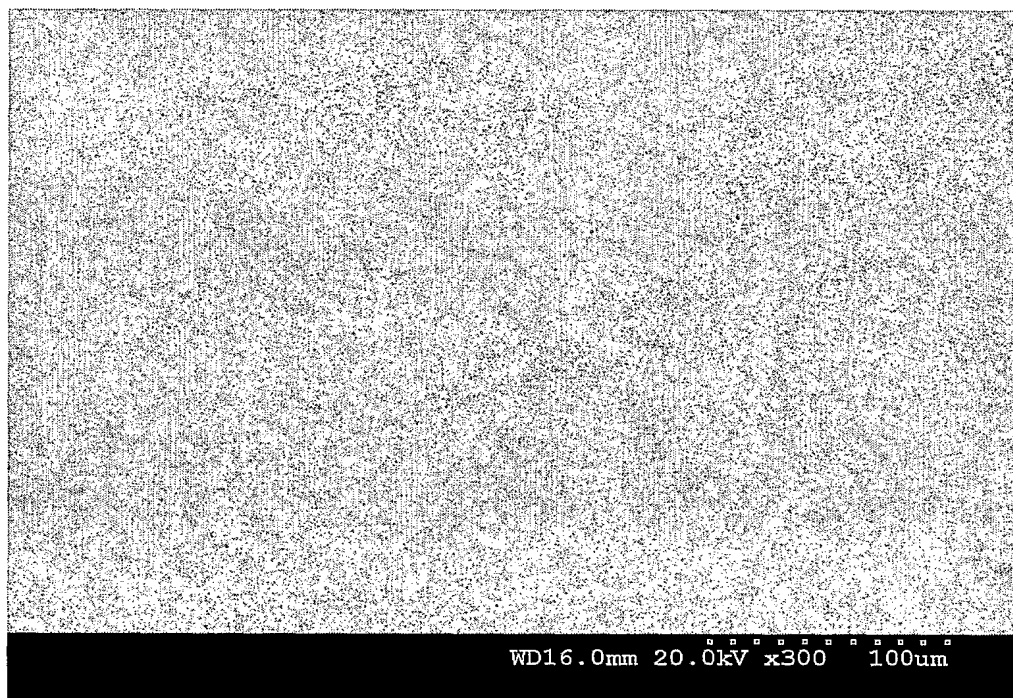
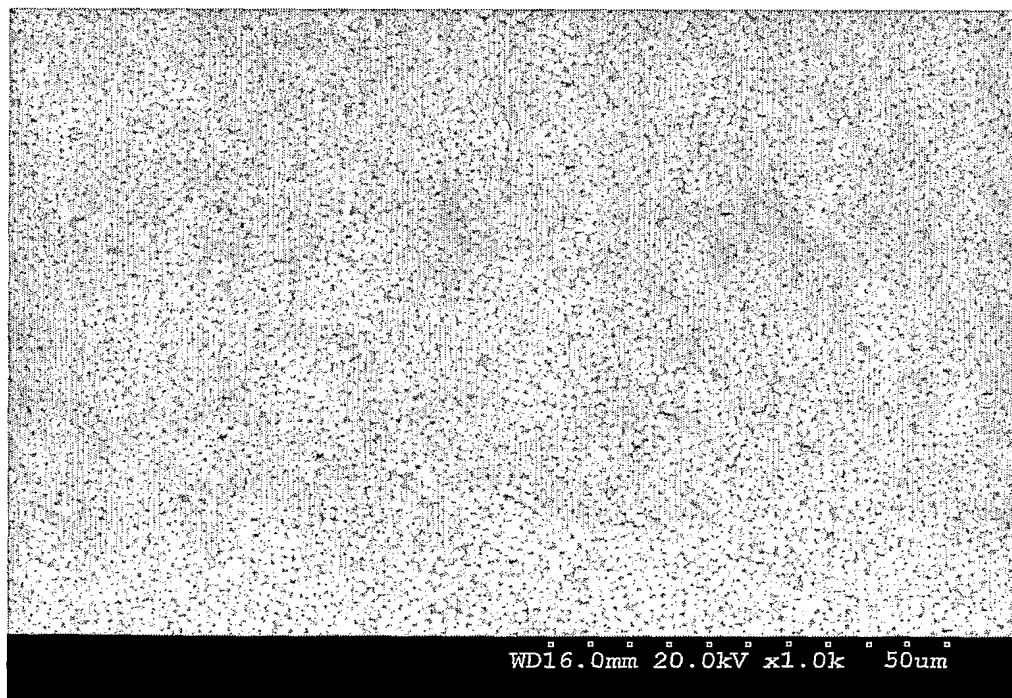


FIGURE 6





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FIGURE 7

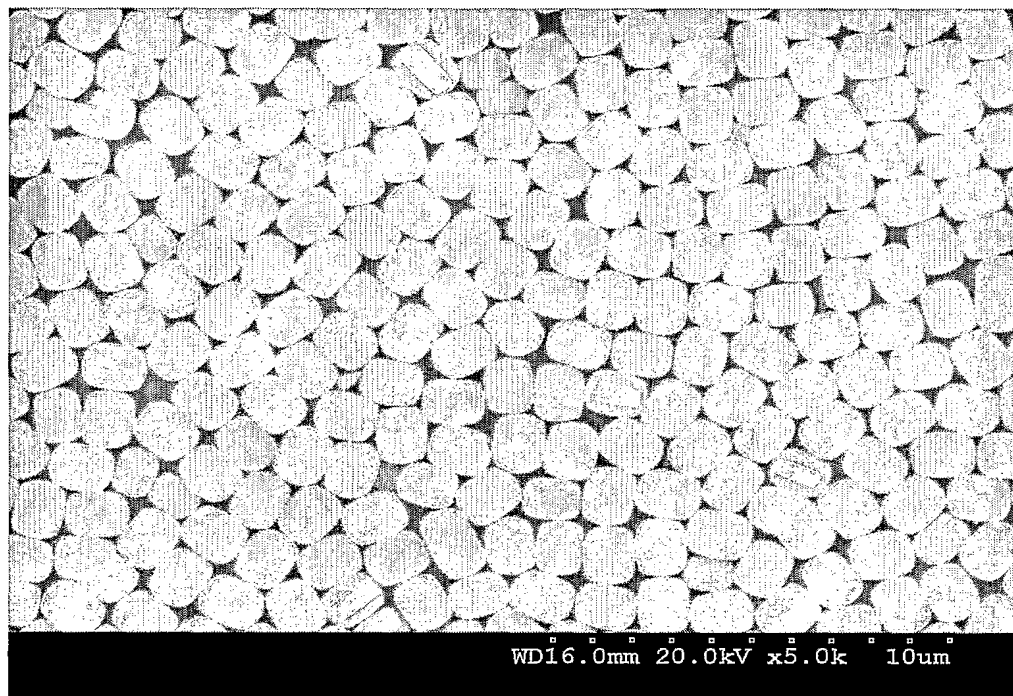
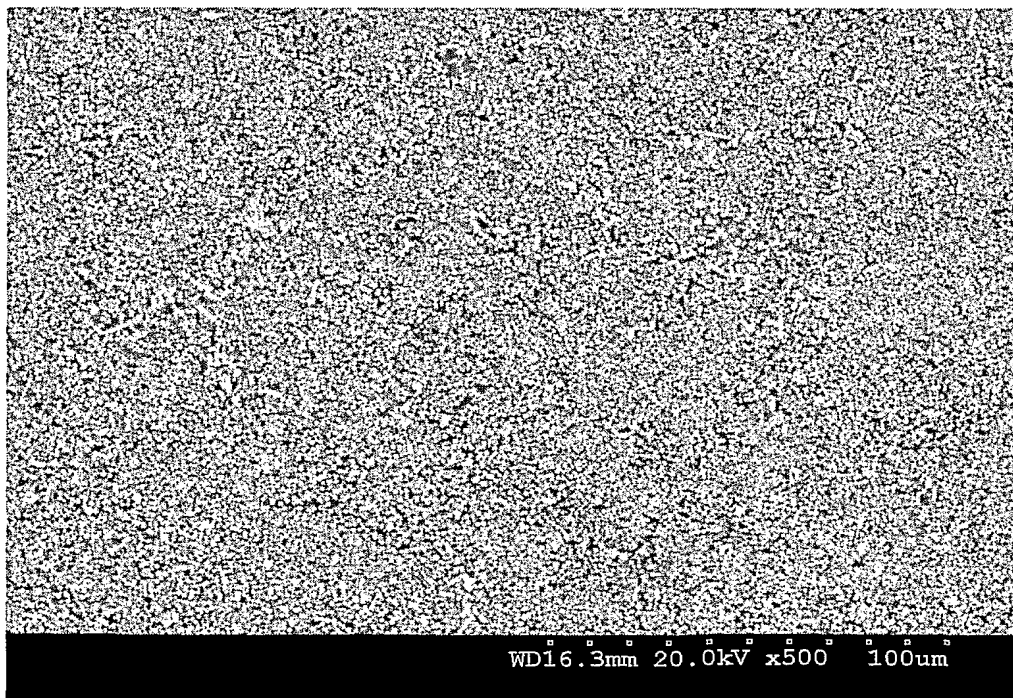


FIGURE 8



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FIGURE 9

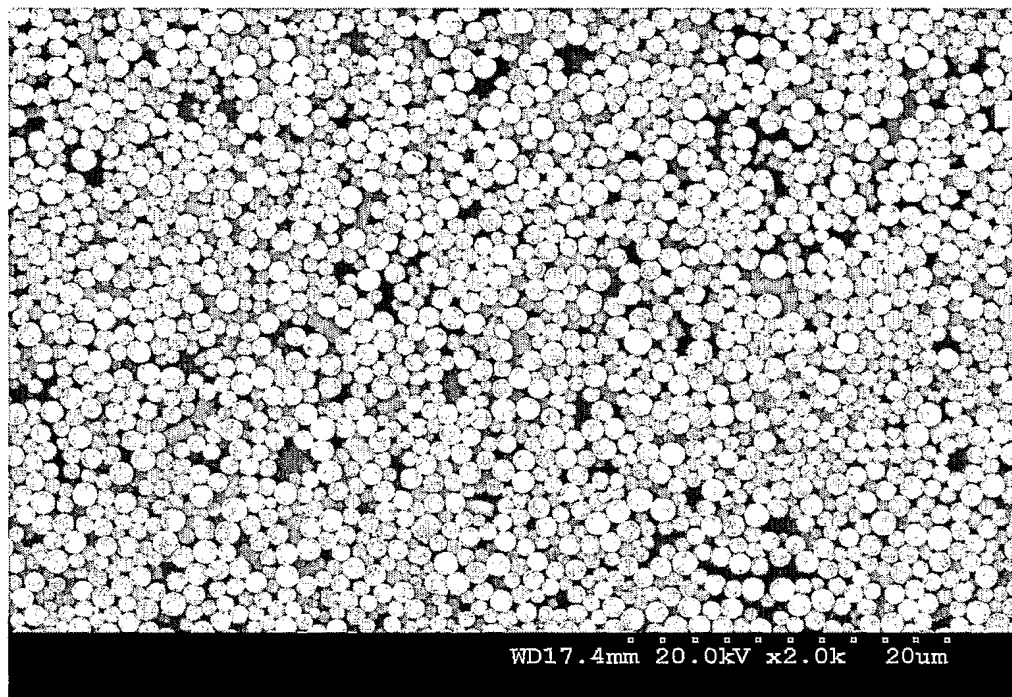
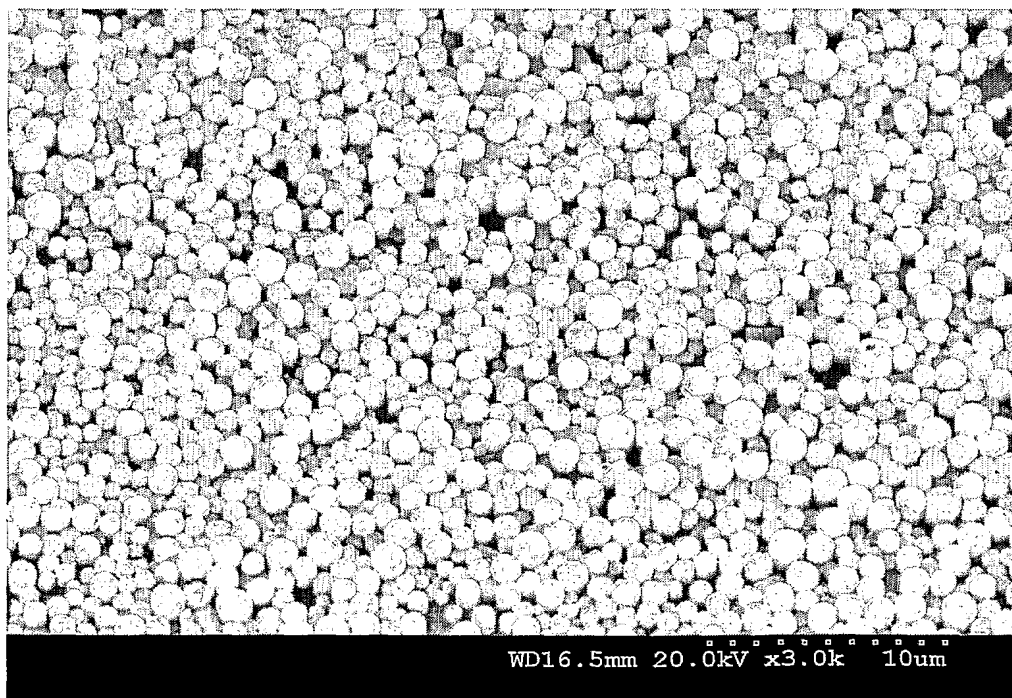


FIGURE 10



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FIGURE 11

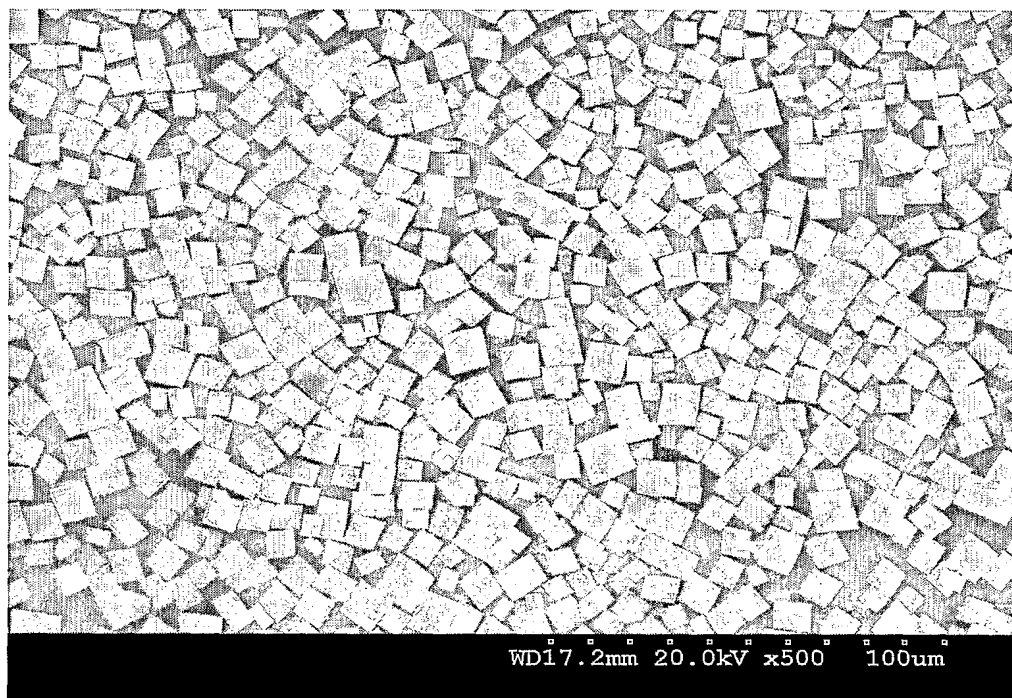
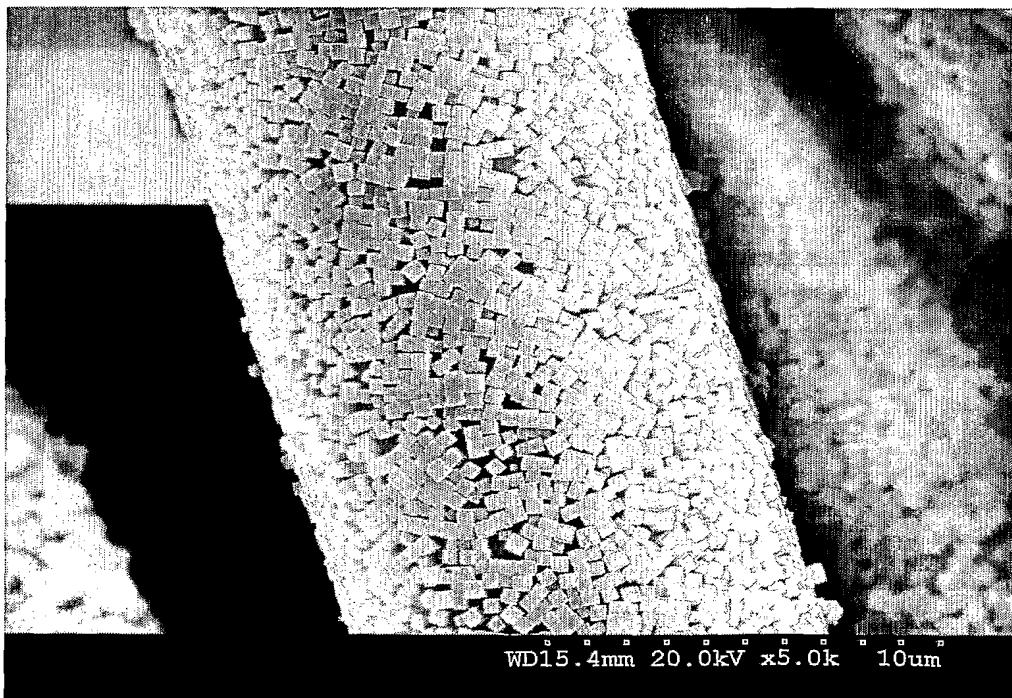


FIGURE 12



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FIGURE 13

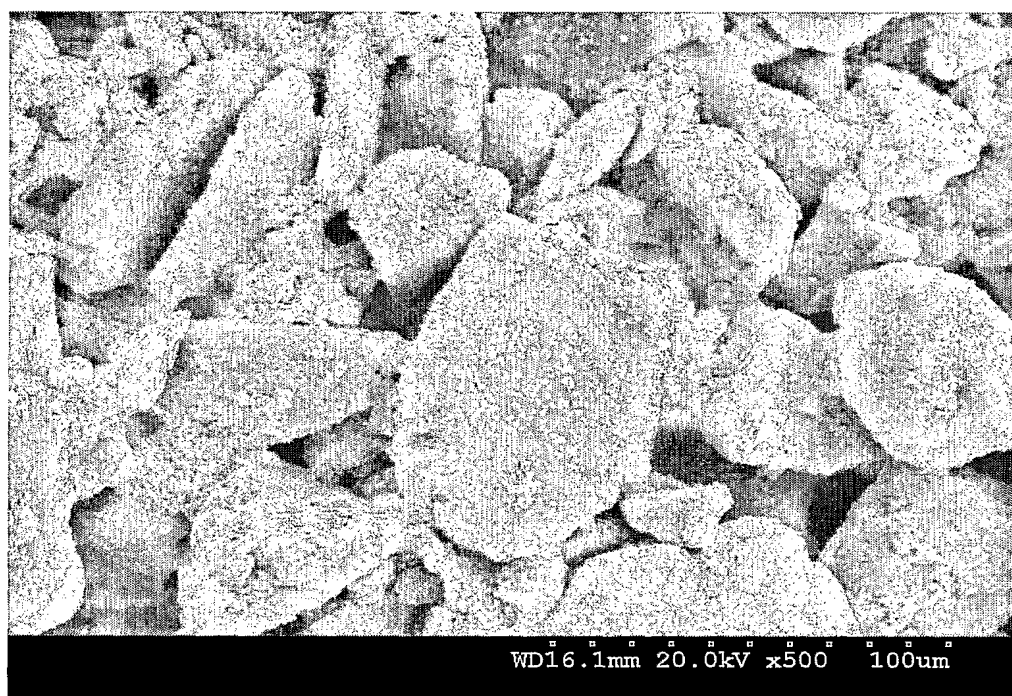
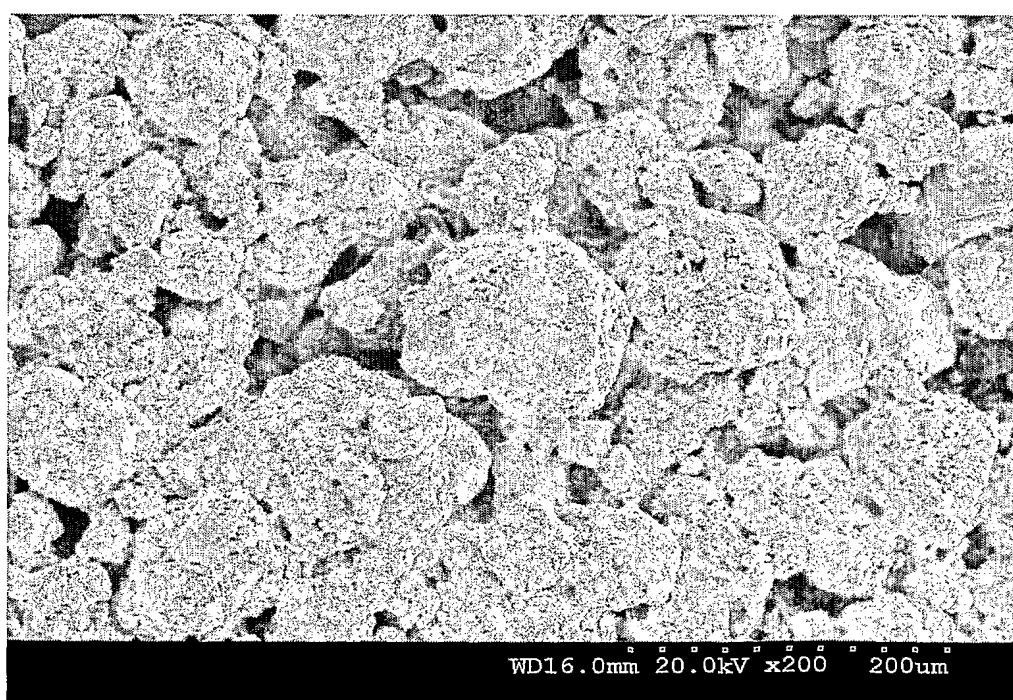


FIGURE 14



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FIGURE 15

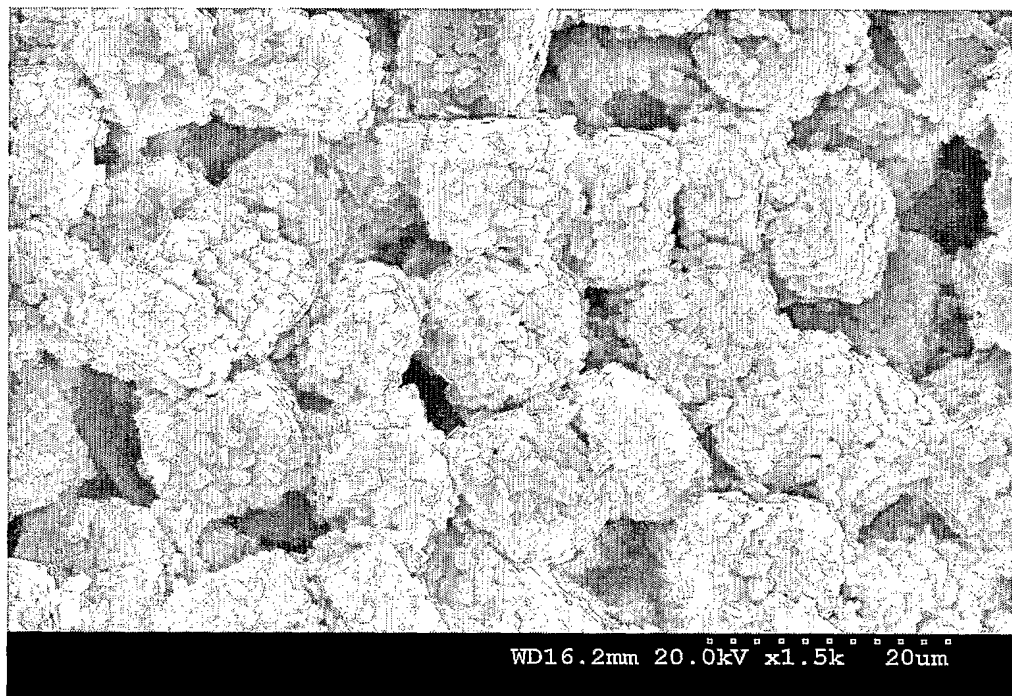
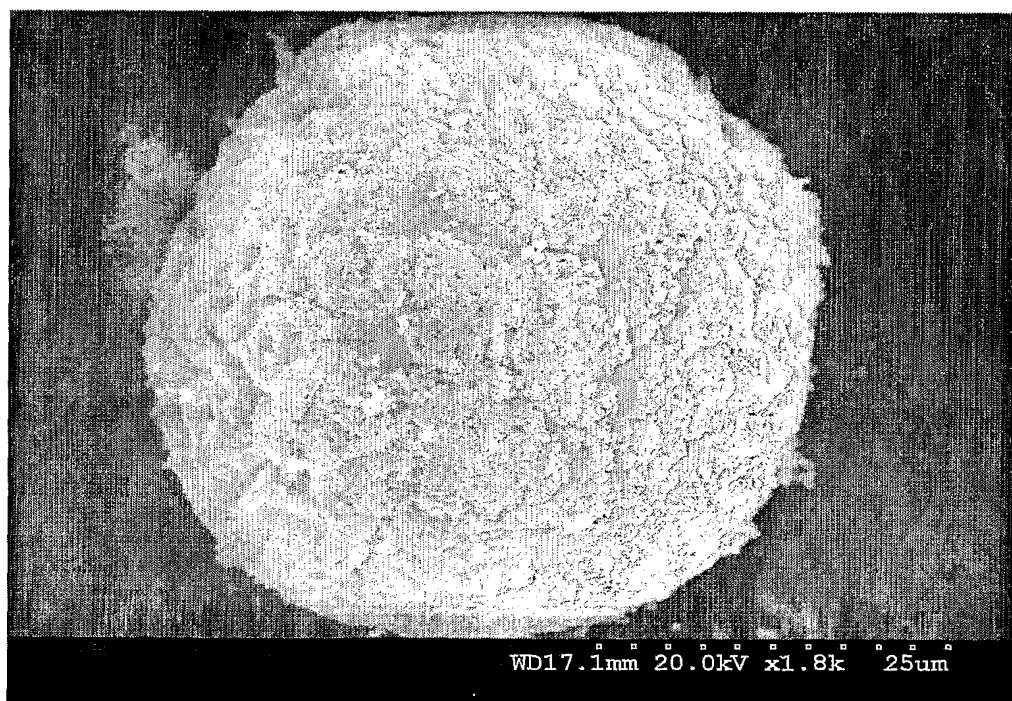


FIGURE 16





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FIGURE 17

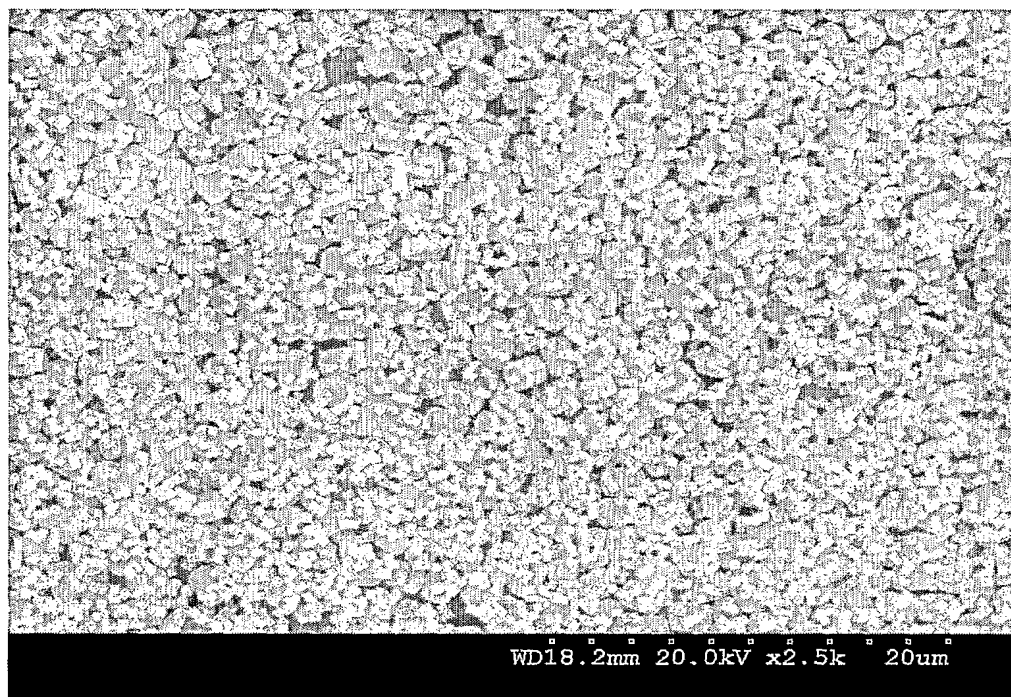
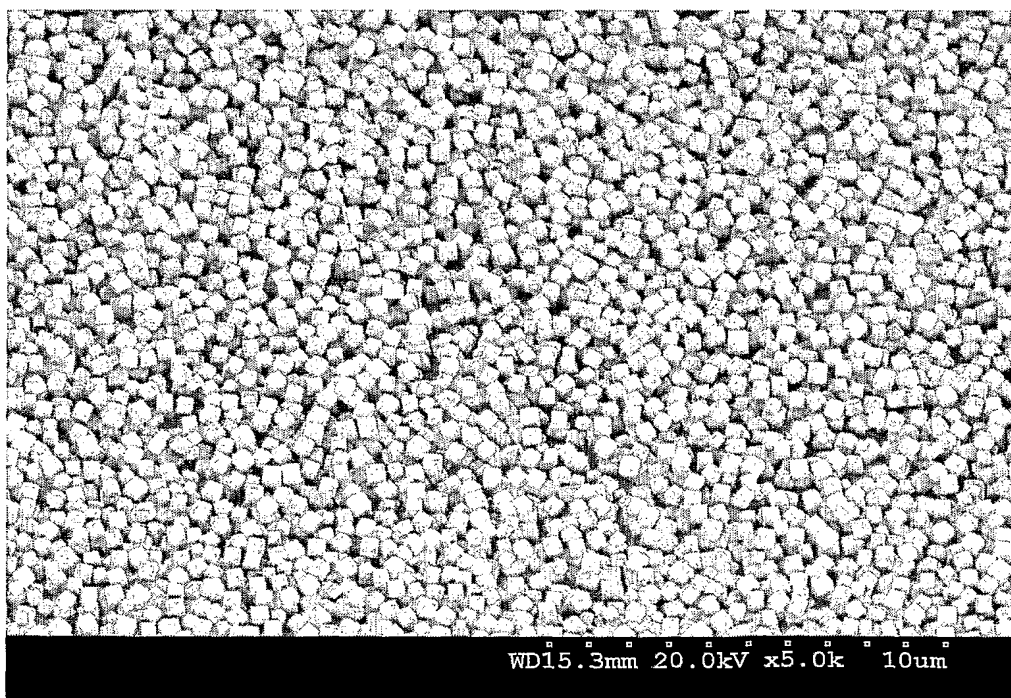


FIGURE 18



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FIGURE 19

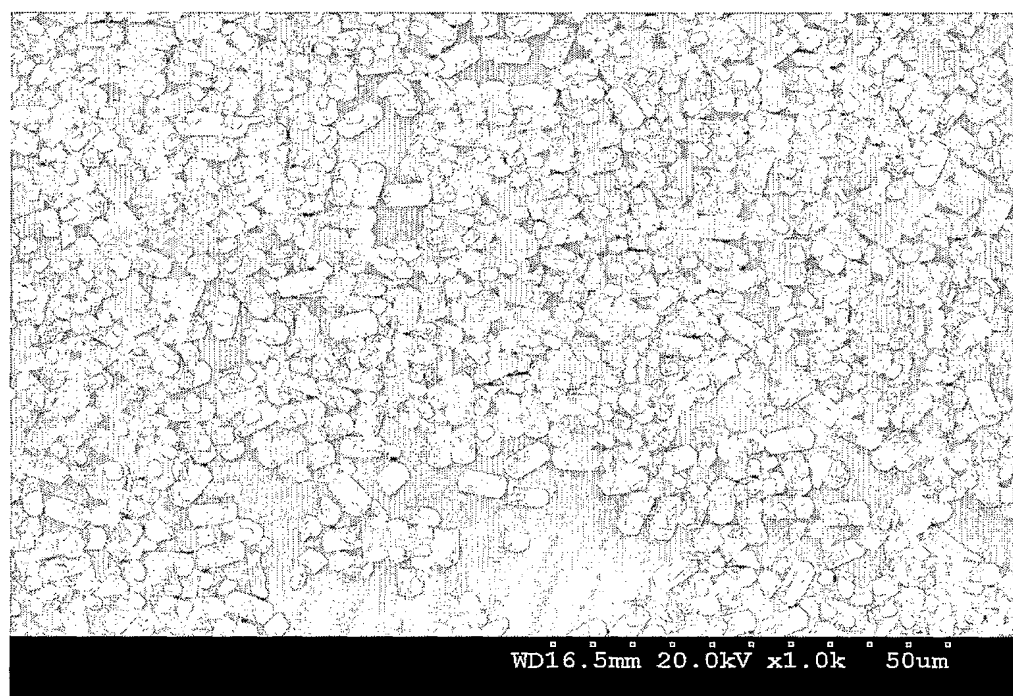
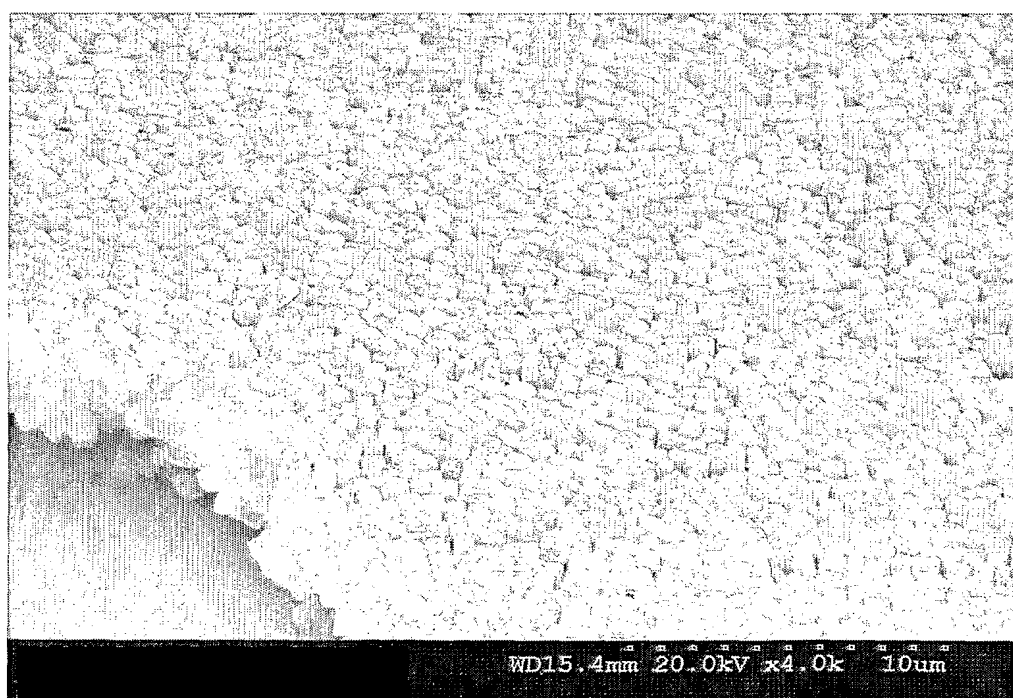


FIGURE 20



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FIGURE 21

Zeolite NaA (powder)

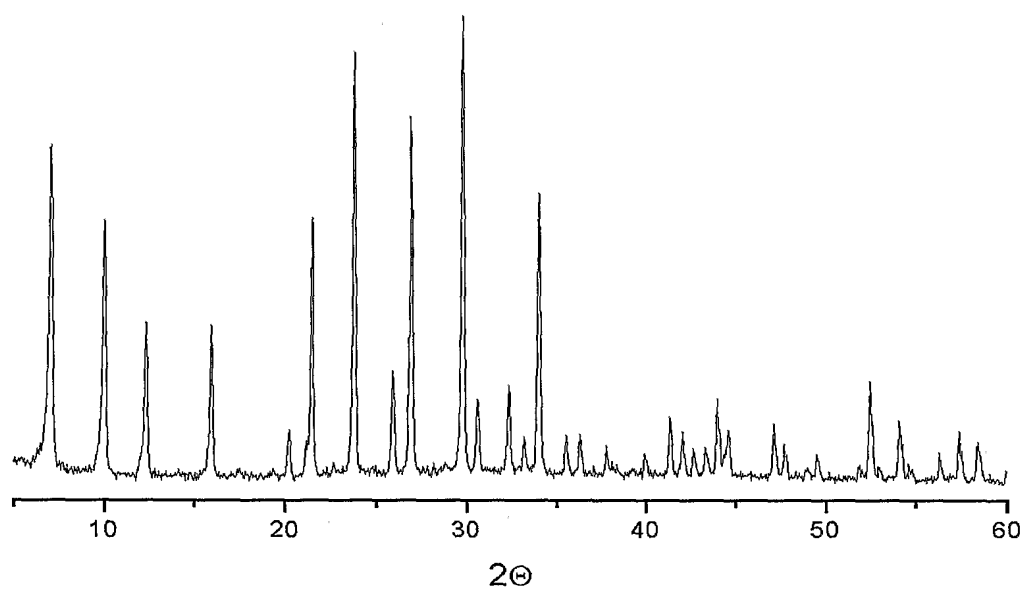
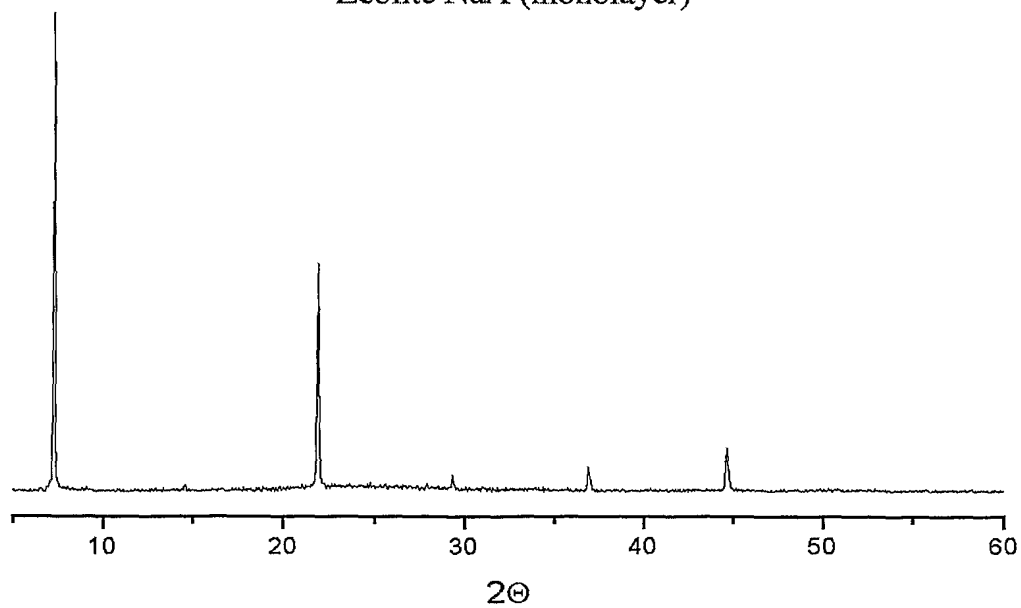


FIGURE 22

Zeolite NaA (monolayer)





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FIGURE 23

Zeolite ZSM-5 (powder)

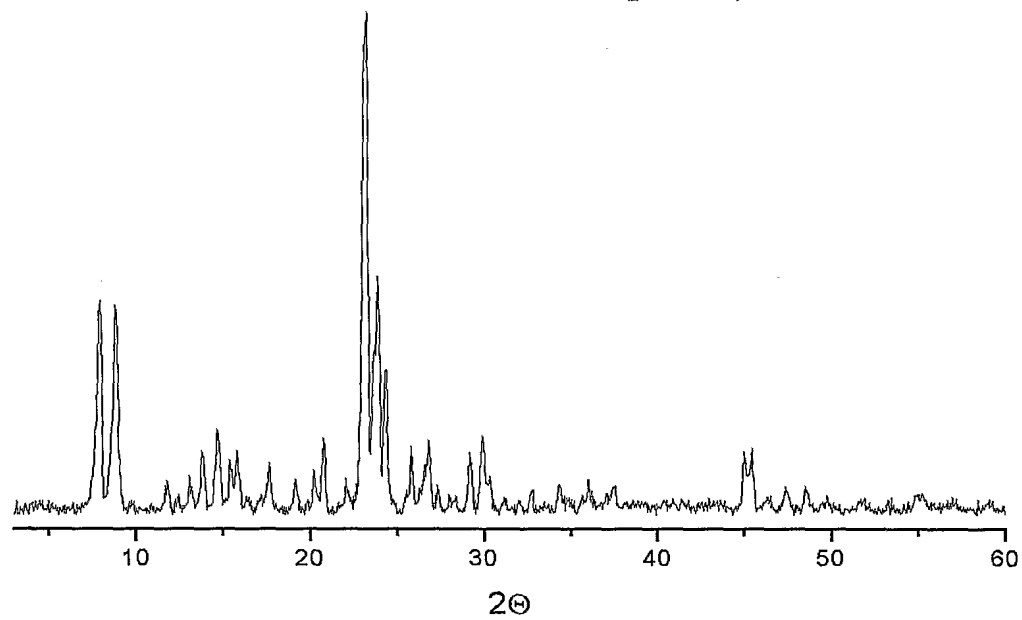
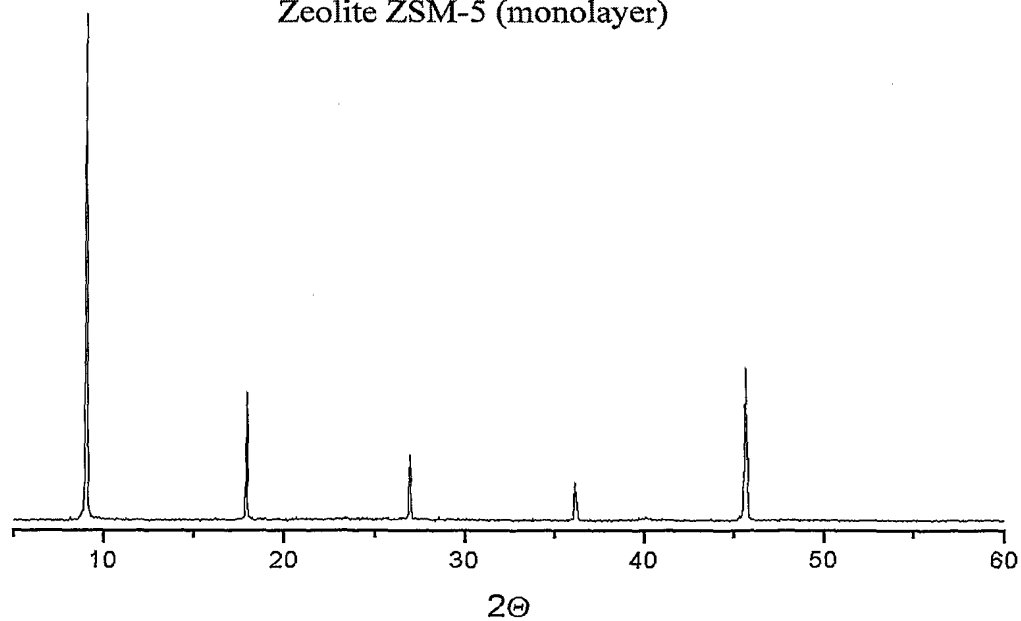


FIGURE 24

Zeolite ZSM-5 (monolayer)



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FIGURE 25

Zeolite KL (powder)

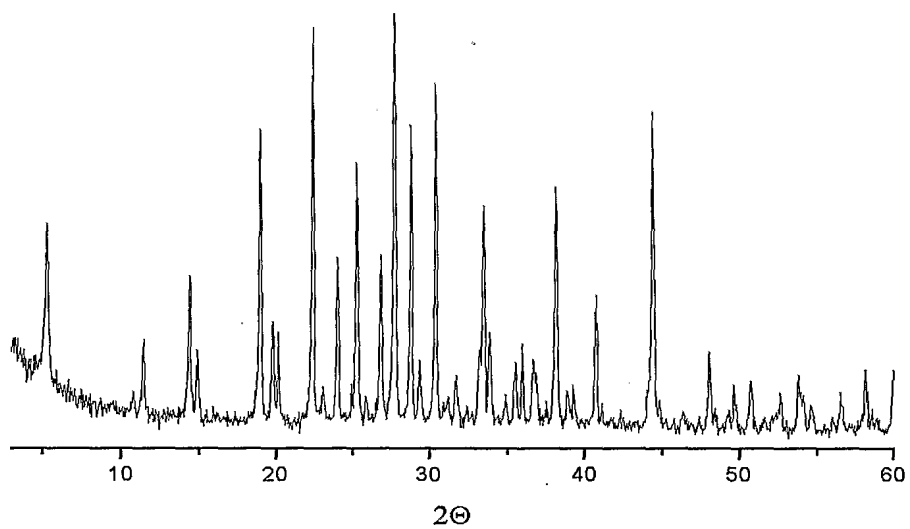
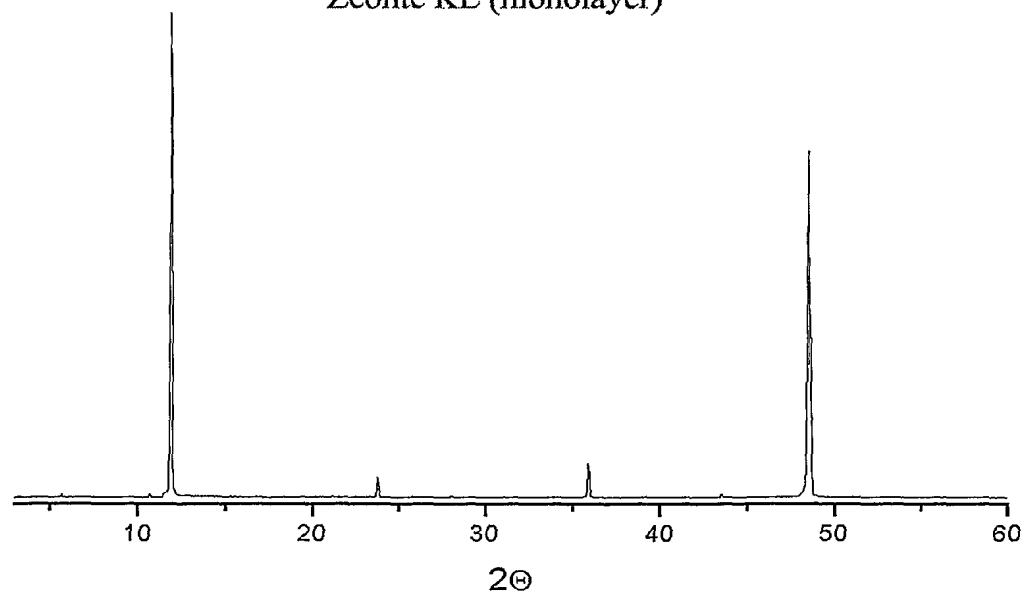


FIGURE 26

Zeolite KL (monolayer)



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FIGURE 27

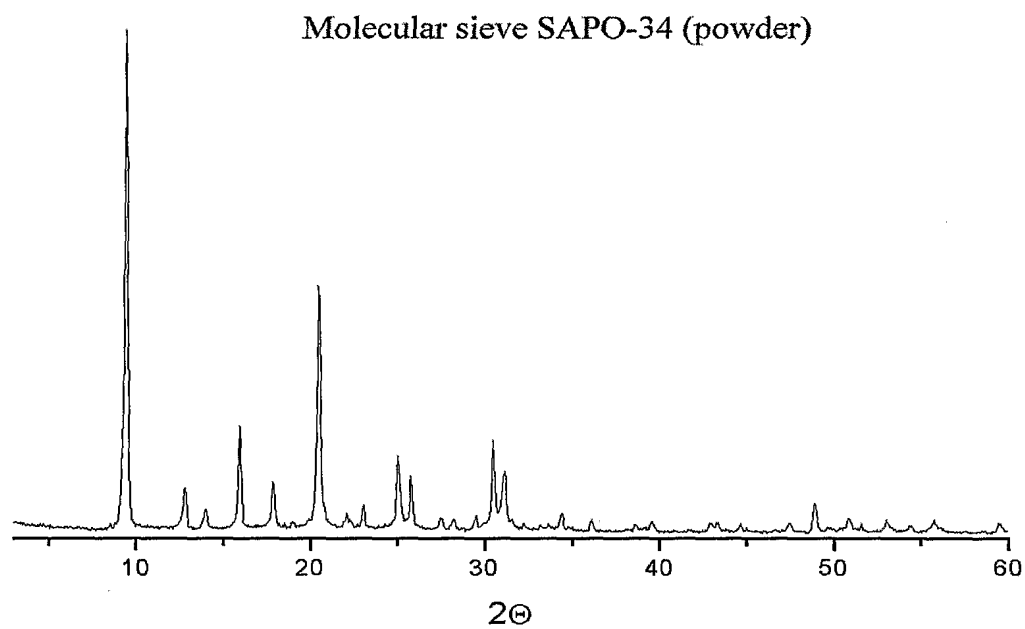
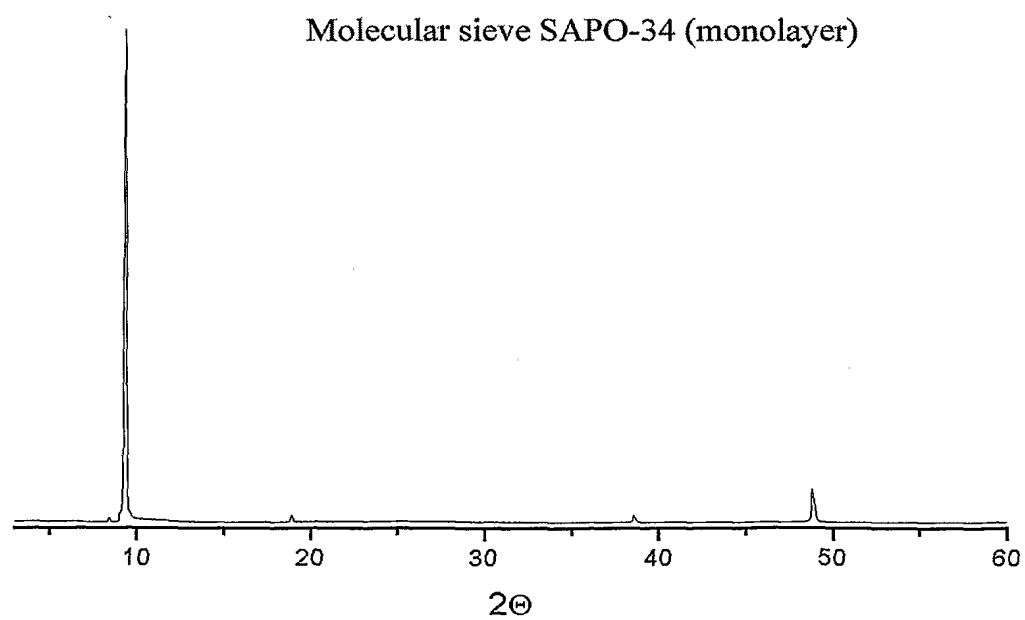


FIGURE 28



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR00/01002

**A. CLASSIFICATION OF SUBJECT MATTER****IPC7 B32B 27/00**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC7 B32B 27/00, B01J 20/28, B01J 31/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patents and Applications for Inventions since 1975

Korean Utility Models and Applications for Utility Models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NPS, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6060415 A (Chao et al.) 9 May 2000 See Whole document	1-4
A	US 6043177 A (Falconer et al.) 28 March 2000 See Whole document	1-4
A	US 6028025 A (Ying et al.) 22 February 2000 See Whole document	1-4
A	KR 99-703 A (Korean Research Institute of Chemical Technology) 15 January 1999 See Whole document	5-7

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 JANUARY 2001 (15.01.2001)

Date of mailing of the international search report

16 JANUARY 2001 (16.01.2001)

Name and mailing address of the ISA/KR

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Metropolitan City 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

LEE, Jung Hee

Telephone No. 82-42-481-5574



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR00/01002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6060415 A	09.05.2000	None	
US 6043177 A	28.03.2000	None	
US 6028025 A	22.02.2000	WO 9817389 A	30.04.98
KR 99-703 A	15.01.1999	None	